Quantum Cluster Methods

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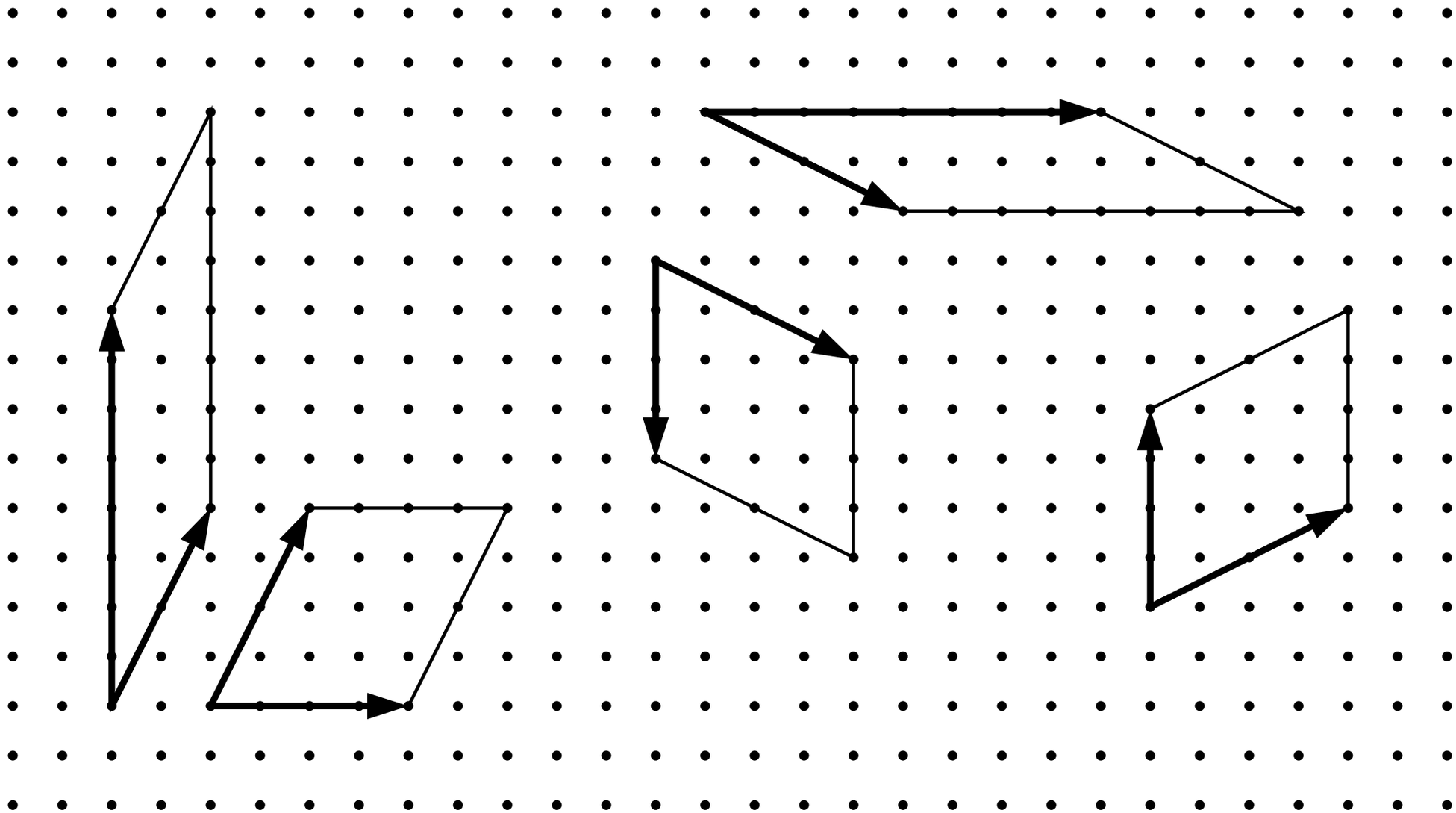

Übungsaufgabe

gegeben
N_e Elektronen, N_i Atomkerne der Masse M_α und Kernladungszahl Z_α,
lösen Sie:

$$H = -\frac{\hbar^2}{2m}\sum_{j=1}^{N_e}\nabla_j^2 - \sum_{\alpha=1}^{N_i}\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 - \frac{1}{4\pi\epsilon_0}\sum_{j=1}^{N_e}\sum_{\alpha=1}^{N_i}\frac{Z_\alpha e^2}{|r_j - R_\alpha|} + \frac{1}{4\pi\epsilon_0}\sum_{j<k}^{N_e}\frac{e^2}{|r_j - r_k|} + \frac{1}{4\pi\epsilon_0}\sum_{\alpha<\beta}^{N_i}\frac{Z_\alpha Z_\beta e^2}{|R_\alpha - R_\beta|}$$

The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

P.M.A Dirac, *Proceedings of the Royal Society* **A123**, 714 (1929)

The Theory of Everything

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Contributed by David Pines, November 18, 1999

We discuss recent developments in our understanding of matter, broadly construed, and their implications for contemporary research in fundamental physics.

The Theory of Everything is a term for the ultimate theory of the universe—a set of equations capable of describing all phenomena that have been observed, or that will ever be observed (1). It is the modern incarnation of the reductionist ideal of the ancient Greeks, an approach to the natural world that has been fabulously successful in bettering the lot of mankind and continues in many people's minds to be the central paradigm of physics. A special case of this idea, and also a beautiful instance of it, is the equation of conventional nonrelativistic quantum mechanics, which describes the everyday world of human beings—air, water, rocks, fire, people, and so forth. The details of this equation are less important than the fact that it can be written down simply and is completely specified by a handful of known quantities: the charge and mass of the electron, the charges and masses of the atomic nuclei, and Planck's constant. For experts we write

$$i\hbar \frac{\partial}{\partial t} |\Psi> = \mathcal{H}|\Psi> \qquad [1]$$

where

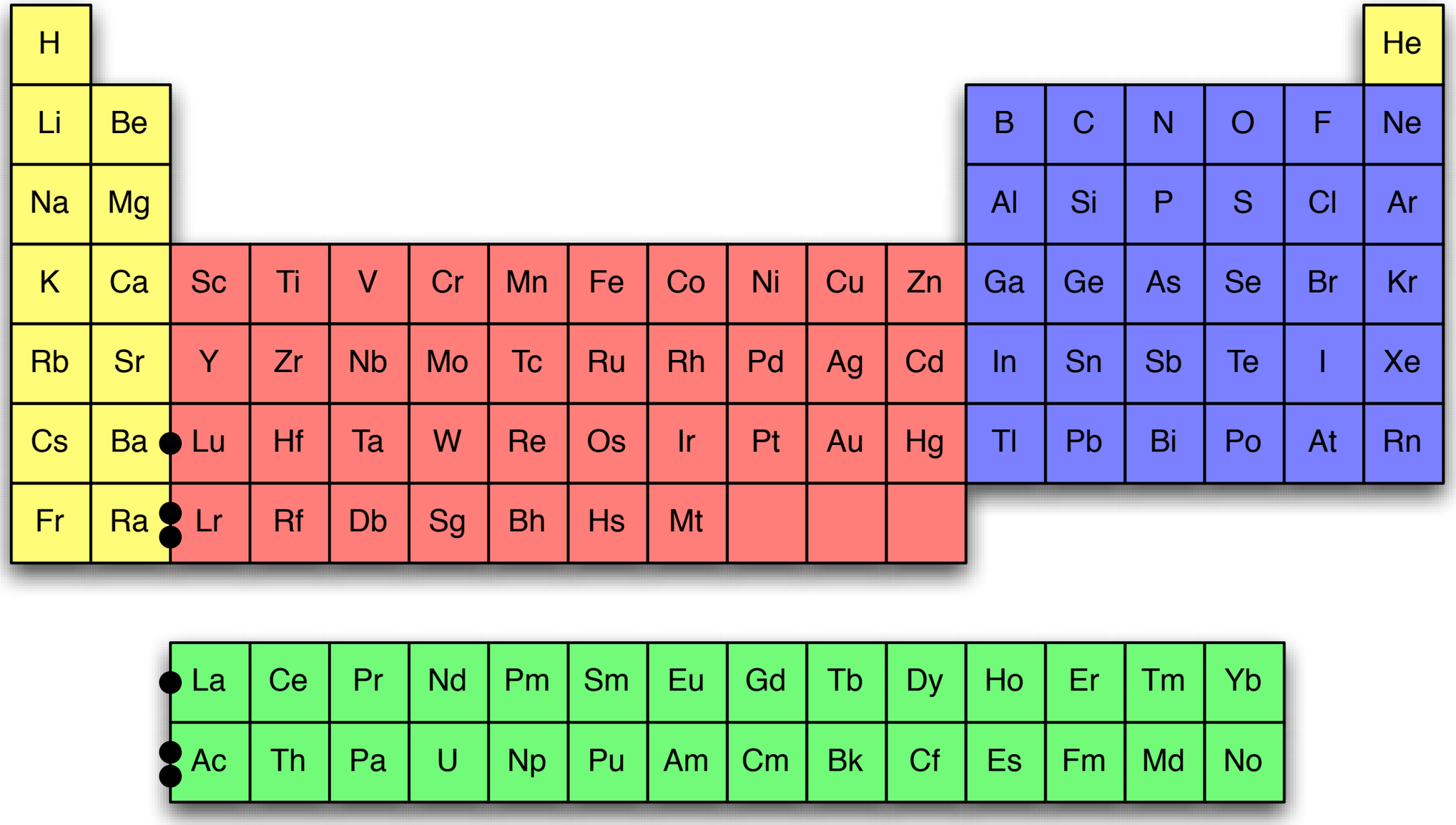
$$\mathcal{H} = -\sum_j^{N_e} \frac{\hbar^2}{2m} \nabla_j^2 - \sum_\alpha^{N_i} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 - \sum_j^{N_e} \sum_\alpha^{N_i} \frac{Z_\alpha e^2}{|\vec{r}_j - \vec{R}_\alpha|} + \sum_{j \ll k}^{N_e} \frac{e^2}{|\vec{r}_j - \vec{r}_k|} + \sum_{\alpha \ll \beta}^{N_i} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{r}_\beta|}. \qquad [2]$$

we have learned why atoms have the size they do, why chemical bonds have the length and strength they do, why solid matter has the elastic properties it does, why some things are transparent while others reflect or absorb light (6). With a little more experimental input for guidance it is even possible to predict atomic conformations of small molecules, simple chemical reaction rates, structural phase transitions, ferromagnetism, and sometimes even superconducting transition temperatures (7). But the schemes for approximating are not first-principles deductions but are rather art keyed to experiment, and thus tend to be the least reliable precisely when reliability is most needed, i.e., when experimental information is scarce, the physical behavior has no precedent, and the key questions have not yet been identified. There are many notorious failures of alleged *ab initio* computation methods, including the phase diagram of liquid ^{3}He and the entire phenomenonology of high-temperature superconductors (8–10). Predicting protein functionality or the behavior of the human brain from these equations is patently absurd. So the triumph of the reductionism of the Greeks is a pyrrhic victory: We have succeeded in reducing all of ordinary physical behavior to a simple, correct Theory of Everything only to discover that it has revealed exactly nothing about many things of great importance.

In light of this fact it strikes a thinking person as odd that the parameters e, $\hbar$, and m appearing in these equations may be measured accurately in laboratory experiments involving large numbers of particles. The electron charge, for example, may be accurately measured by passing current through an electrochemical cell, plating out metal atoms, and measuring the mass deposited, the separation of the atoms in the crystal being known from x-ray diffraction (11). Simple electrical measurements performed on superconducting rings determine to high accuracy the quantity the quantum of magnetic flux $hc/2e$ (11). A version

most important question

what atoms to pick?
what materials are *interesting*?



simpler question

electronic Hamiltonian in Born-Oppenheimer approximation

$$H = -\frac{1}{2}\sum_{j=1}^{N_e}\nabla_j^2 - \sum_{j=1}^{N_e}\sum_{\alpha=1}^{N_i}\frac{Z_\alpha}{|r_j - R_\alpha|} + \sum_{j<k}^{N_e}\frac{1}{|r_j - r_k|} + \sum_{\alpha<\beta}^{N_i}\frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}$$

given a material $\{ Z_\alpha, R_\alpha \}$
solve

$$H\Psi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) = E\Psi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$$

antisymmetrize wavefunction

antisymmetric wave-functions

(anti)symmetrization of N-body wave-function: $N!$ operations

$$\mathcal{S}_\pm \, \psi(x_1, \ldots, x_N) := \frac{1}{\sqrt{N!}} \sum_P (\pm 1)^P \psi\left(x_{p(1)}, \ldots, x_{p(N)}\right)$$

antisymmetrization of products of single-particle states

$$\mathcal{S}_- \, \varphi_{\alpha_1}(x_1) \cdots \varphi_{\alpha_N}(x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}$$

much more efficient: scales only polynomially in N

Slater determinant: $\Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N)$

Slater determinants

$$\Phi_{\alpha_1 \cdots \alpha_N}(\mathbf{x}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}$$

simple examples

N=1: $\Phi_{\alpha_1}(x_1) = \varphi_{\alpha_1}(x_1)$

N=2: $\Phi_{\alpha_1\alpha_2}(x_1, x_2) = \frac{1}{\sqrt{2}}\left(\varphi_{\alpha_1}(x_1)\varphi_{\alpha 2}(x_2) - \varphi_{\alpha_2}(x_1)\varphi_{\alpha_1}(x_2)\right)$

expectation values need only one antisymmetrized wave-function:

$$\int d\mathbf{x}\, \overline{(\mathcal{S}_\pm \Psi_a(\mathbf{x}))}\, M(\mathbf{x})\, (\mathcal{S}_\pm \Psi_b(\mathbf{x})) = \int d\mathbf{x} \left(\sqrt{N!}\, \overline{\Psi_a(\mathbf{x})}\right) M(\mathbf{x})\, (\mathcal{S}_\pm \Psi_b(\mathbf{x}))$$

remember: $M(x_1, \ldots, x_N)$ symmetric in arguments

corollary: overlap of Slater determinants:

$$\int dx_1 \cdots dx_N\, \overline{\Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N)}\, \Phi_{\beta_1 \cdots \beta_N}(x_1, \ldots, x_N) = \det\left(\langle \varphi_{\alpha_n} | \varphi_{\beta_m} \rangle\right)$$

basis of Slater determinants

$$\int dx_1 \cdots dx_N \, \overline{\Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N)} \, \Phi_{\beta_1 \cdots \beta_N}(x_1, \ldots, x_N) = \det\Big(\langle \varphi_{\alpha_n} | \varphi_{\beta_m} \rangle \Big)$$

Slater determinants of ortho-normal orbitals $\varphi_a(x)$ are normalized

a Slater determinant with two identical orbital indices vanishes (Pauli principle)

Slater determinants that only differ in the order of the orbital indices are (up to a sign) identical

define **convention for ordering indices**, e.g. $\alpha_1 < \alpha_2 < \ldots < \alpha_N$

given K (ortho-normal orbitals) $\{ \varphi_a(x) \mid \alpha \in \{1, \ldots, K\} \}$

the $K! \,/\, N! \, (K-N)!$ Slater determinants

$$\Big\{ \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \ldots, x_N) \,\Big|\, \alpha_1 < \alpha_2 < \cdots < \alpha_N \in \{1, \ldots, K\} \Big\}$$

are an (ortho-normal) basis of the N-electron Hilbert space

second quantization: motivation

keeping track of all these signs...

Slater determinant $\Phi_{\alpha\beta}(x_1, x_2) = \frac{1}{\sqrt{2}} \left(\varphi_\alpha(x_1)\varphi_\beta(x_2) - \varphi_\beta(x_1)\varphi_\alpha(x_2)\right)$

corresponding Dirac state $|\alpha, \beta\rangle = \frac{1}{\sqrt{2}} \left(|\alpha\rangle|\beta\rangle - |\beta\rangle|\alpha\rangle\right)$

use operators $|\alpha, \beta\rangle = c_\beta^\dagger c_\alpha^\dagger |0\rangle$

position of operators encodes signs

$$c_\beta^\dagger c_\alpha^\dagger |0\rangle = |\alpha, \beta\rangle = -|\beta, \alpha\rangle = -c_\alpha^\dagger c_\beta^\dagger |0\rangle$$

product of operators changes sign when commuted: anti-commutation

anti-commutator $\{A, B\} := A\,B + B\,A$

second quantization: motivation

specify *N*-electron states using operators

N=0: $|0\rangle$ (vacuum state)

normalization: $\langle 0|0\rangle = 1$

N=1: $|\alpha\rangle = c_\alpha^\dagger|0\rangle$ (creation operator adds one electron)

normalization: $\langle\alpha|\alpha\rangle = \langle 0|c_\alpha c_\alpha^\dagger|0\rangle$

overlap: $\langle\alpha|\beta\rangle = \langle 0|c_\alpha c_\beta^\dagger|0\rangle$

adjoint of creation operator removes one electron: annihilation operator

$$c_\alpha|0\rangle = 0 \text{ and } c_\alpha c_\beta^\dagger = \pm c_\beta^\dagger c_\alpha + \langle\alpha|\beta\rangle$$

N=2: $|\alpha,\beta\rangle = c_\beta^\dagger c_\alpha^\dagger|0\rangle$

antisymmetry: $c_\alpha^\dagger c_\beta^\dagger = -c_\beta^\dagger c_\alpha^\dagger$

second quantization: formalism

vacuum state $|0\rangle$

and

set of operators c_α related to single-electron states $\varphi_\alpha(x)$

defined by:

$$c_\alpha|0\rangle = 0 \qquad \left\{c_\alpha, c_\beta\right\} = 0 = \left\{c_\alpha^\dagger, c_\beta^\dagger\right\}$$

$$\langle 0|0\rangle = 1 \qquad \left\{c_\alpha, c_\beta^\dagger\right\} = \langle\alpha|\beta\rangle$$

see also
www.cond-mat.de/events/correl13/manuscripts/koch.pdf

second quantization: field operators

creation/annihilation operators in real-space basis

$\hat{\psi}^\dagger(x)$ with $x = (r, \sigma)$ creates electron of spin σ at position r

$$\text{then} \quad c_\alpha^\dagger = \int dx\, \varphi_\alpha(x) \hat{\psi}^\dagger(x)$$

put electron at x with amplitude $\varphi_a(x)$

$\{\varphi_{\alpha_n}(x)\}$ complete orthonormal set $\sum_j \overline{\varphi_{\alpha_j}(x)}\, \varphi_{\alpha_j}(x') = \delta(x - x')$

$$\hat{\psi}(x) = \sum_n \varphi_{\alpha_n}(x)\, c_{\alpha_n}$$

they fulfill the standard anti-commutation relations

$$\left\{\hat{\psi}(x), \hat{\psi}(x')\right\} = 0 = \left\{\hat{\psi}^\dagger(x), \hat{\psi}^\dagger(x')\right\}$$
$$\left\{\hat{\psi}(x), \hat{\psi}^\dagger(x')\right\} = \delta(x - x')$$

second quantization: Slater determinants

$$\Phi_{\alpha_1\alpha_2\ldots\alpha_N}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \left\langle 0 \left| \hat{\psi}(x_1)\hat{\psi}(x_2)\ldots\hat{\psi}(x_N)\, c^\dagger_{\alpha_N} \ldots c^\dagger_{\alpha_2} c^\dagger_{\alpha_1} \right| 0 \right\rangle$$

proof by induction

N=0: $\Phi() = \langle 0|0\rangle = 1$

N=1: $\left\langle 0 \left| \hat{\psi}(x_1)\, c^\dagger_{\alpha_1} \right| 0 \right\rangle = \left\langle 0 \left| \varphi_{\alpha_1}(x_1) - c^\dagger_{\alpha_1}\hat{\psi}(x_1) \right| 0 \right\rangle = \varphi_{\alpha_1}(x_1)$

using $\{\hat{\psi}(x), c^\dagger_\alpha\} = \int dx'\, \varphi_\alpha(x') \left\{\hat{\psi}(x), \hat{\psi}^\dagger(x')\right\} = \varphi_\alpha(x)$

N=2: $\left\langle 0 \left| \hat{\psi}(x_1)\hat{\psi}(x_2)\, c^\dagger_{\alpha_2} c^\dagger_{\alpha_1} \right| 0 \right\rangle$

$$= \left\langle 0 \left| \hat{\psi}(x_1) \left(\varphi_{\alpha_2}(x_2) - c^\dagger_{\alpha_2}\hat{\psi}(x_2)\right) c^\dagger_{\alpha_1} \right| 0 \right\rangle$$

$$= \left\langle 0 \left| \hat{\psi}(x_1) c^\dagger_{\alpha_1} \right| 0 \right\rangle \varphi_{\alpha_2}(x_2) - \left\langle 0 \left| \hat{\psi}(x_1) c^\dagger_{\alpha_2} \hat{\psi}(x_2) c^\dagger_{\alpha_1} \right| 0 \right\rangle$$

$$= \varphi_{\alpha_1}(x_1)\varphi_{\alpha_2}(x_2) - \varphi_{\alpha_2}(x_1)\varphi_{\alpha_1}(x_2)$$

second quantization: Slater determinants

general N: commute $\Psi(x_N)$ to the right

$$\left\langle 0 \left| \hat{\psi}(x_1) \ldots \hat{\psi}(x_{N-1}) \hat{\psi}(x_N)\, c^\dagger_{\alpha_N} c^\dagger_{\alpha_{N-1}} \ldots c^\dagger_{\alpha_1} \right| 0 \right\rangle \;=$$

$$+ \quad \left\langle 0 \left| \hat{\psi}(x_1) \ldots \hat{\psi}(x_{N-1})\, c^\dagger_{\alpha_{N-1}} \ldots c^\dagger_{\alpha_1} \right| 0 \right\rangle \quad \varphi_{\alpha_N}(x_N)$$

$$- \quad \left\langle 0 \left| \hat{\psi}(x_1) \ldots \hat{\psi}(x_{N-1}) \prod_{n \neq N-1} c^\dagger_{\alpha_n} \right| 0 \right\rangle \quad \varphi_{\alpha_{N-1}}(x_N)$$

$$\vdots$$

$$(-1)^N \quad \left\langle 0 \left| \hat{\psi}(x_1) \ldots \hat{\psi}(x_{N-1})\, c^\dagger_{\alpha_N} \quad \ldots \quad c^\dagger_{\alpha_2} \right| 0 \right\rangle \quad \varphi_{\alpha_1}(x_N)$$

Laplace expansion in terms of *N-1* dim determinants wrt last row of

$$= \begin{vmatrix} \varphi_{\alpha_1}(x_1) & \varphi_{\alpha_2}(x_1) & \cdots & \varphi_{\alpha_N}(x_1) \\ \varphi_{\alpha_1}(x_2) & \varphi_{\alpha_2}(x_2) & \cdots & \varphi_{\alpha_N}(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha_1}(x_N) & \varphi_{\alpha_2}(x_N) & \cdots & \varphi_{\alpha_N}(x_N) \end{vmatrix}$$

second quantization: Dirac notation

product state $c^\dagger_{\alpha_N} \cdots c^\dagger_{\alpha_2} c^\dagger_{\alpha_1} |0\rangle$

corresponds to

Slater determinant $\Phi_{\alpha_1 \alpha_2 \ldots \alpha_N}(x_1, x_2, \ldots, x_N)$

as

Dirac state $|\alpha\rangle$

corresponds to

wave-function $\varphi_\alpha(x)$

second quantization: expectation values

expectation value of *N*-body operator wrt *N*-electron Slater determinants

$$\int dx_1 \cdots dx_N \, \overline{\Phi_{\beta_1 \cdots \beta_N}(x_1, \cdots, x_N)} M(x_1, \cdots, x_N) \Phi_{\alpha_1 \cdots \alpha_N}(x_1, \cdots, x_N)$$

$$= \left\langle 0 \left| c_{\beta_1} \cdots c_{\beta_N} \, \hat{M} \, c^\dagger_{\alpha_N} \cdots c^\dagger_{\alpha_1} \right| 0 \right\rangle$$

$$\int dx_1 \cdots dx_N \frac{1}{\sqrt{N!}} \left\langle 0 \left| c_{\beta_1} \cdots c_{\beta_N} \, \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) \right| 0 \right\rangle M(x_1, \cdots, x_N) \frac{1}{\sqrt{N!}} \left\langle 0 \left| \hat{\psi}(x_1) \cdots \hat{\psi}(x_N) \, c^\dagger_{\alpha_N} \cdots c^\dagger_{\alpha_1} \right| 0 \right\rangle$$

$$= \left\langle 0 \left| c_{\beta_1} \cdots c_{\beta_N} \, \frac{1}{N!} \int dx_1 \cdots dx_N \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) M(x_1, \cdots, x_N) \hat{\psi}(x_1) \cdots \hat{\psi}(x_N) \, c^\dagger_{\alpha_N} \cdots c^\dagger_{\alpha_1} \right| 0 \right\rangle$$

$|0\rangle\langle 0| = \mathbb{1}$ on 0-electron space

collecting field-operators to obtain *M* in second quantization:

$$\hat{M} = \frac{1}{N!} \int dx_1 \cdots x_N \, \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) \, M(x_1, \cdots, x_N) \, \hat{\psi}(x_1) \cdots \hat{\psi}(x_N)$$

apparently dependent on number *N* of electrons!

second quantization: zero-body operator

zero-body operator $M_0(x_1,\ldots x_N)$=1 independent of particle coordinates

second quantized form for operating on N-electron states:

$$\hat{M}_0 = \frac{1}{N!}\int dx_1 dx_2 \cdots x_N \, \hat{\psi}^\dagger(x_N)\cdots\hat{\psi}^\dagger(x_2)\hat{\psi}^\dagger(x_1)\,\hat{\psi}(x_1)\hat{\psi}(x_2)\cdots\hat{\psi}(x_N)$$

$$= \frac{1}{N!}\int \quad dx_2 \cdots x_N \, \hat{\psi}^\dagger(x_N)\cdots\hat{\psi}^\dagger(x_2) \qquad \hat{N} \qquad \hat{\psi}(x_2)\cdots\hat{\psi}(x_N)$$

$$= \frac{1}{N!}\int \quad dx_2 \cdots x_N \, \hat{\psi}^\dagger(x_N)\cdots\hat{\psi}^\dagger(x_2) \qquad 1 \qquad \hat{\psi}(x_2)\cdots\hat{\psi}(x_N)$$

$$\vdots$$

$$= \frac{1}{N!}\, 1\cdot 2 \;\cdots\; N = 1$$

only(!) when operating on N-electron state

using $\int dx\, \hat{\psi}^\dagger(x)\hat{\psi}(x) = \hat{N}$

result independent of N

second quantization: one-body operators

one-body operator $M(x_1, \ldots, x_N) = \sum_j M_1(x_j)$

$$\hat{M}_1 = \frac{1}{N!} \int dx_1 \cdots dx_N \, \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) \sum_j M_1(x_j) \; \hat{\psi}(x_1) \cdots \hat{\psi}(x_N)$$

$$= \frac{1}{N!} \sum_j \int dx_j \, \hat{\psi}^\dagger(x_j) \, M_1(x_j) \, (N-1)! \; \hat{\psi}(x_j)$$

$$= \frac{1}{N} \sum_j \int dx_j \, \hat{\psi}^\dagger(x_j) \, M_1(x_j) \, \hat{\psi}(x_j)$$

$$= \int dx \quad \hat{\psi}^\dagger(x) \;\; M_1(x) \;\; \hat{\psi}(x)$$

result independent of N

expand in complete orthonormal set of orbitals

$$\hat{M}_1 = \sum_{n,m} \int dx \, \overline{\varphi_{\alpha_n}(x)} \, M(x) \, \varphi_{\alpha_m}(x) \; c^\dagger_{\alpha_n} c_{\alpha_m} = \sum_{n,m} \langle \alpha_n | M_1 | \alpha_m \rangle \; c^\dagger_{\alpha_n} c_{\alpha_m}$$

second quantization: two-body operators

two-body operator $M(x_1, \ldots, x_N) = \sum_{i<j} M_2(x_i, x_j)$

$$\hat{M}_2 = \frac{1}{N!} \int dx_1 \cdots dx_N \, \hat{\psi}^\dagger(x_N) \cdots \hat{\psi}^\dagger(x_1) \sum_{i<j} M_2(x_i, x_j) \; \hat{\psi}(x_1) \cdots \hat{\psi}(x_N)$$

$$= \frac{1}{N!} \sum_{i<j} \int dx_i dx_j \, \hat{\psi}^\dagger(x_j) \hat{\psi}^\dagger(x_i) \, M_2(x_i, x_j) \, (N-2)! \; \hat{\psi}(x_i) \hat{\psi}(x_j)$$

$$= \frac{1}{N(N-1)} \sum_{i<j} \int dx_i dx_j \, \hat{\psi}^\dagger(x_j) \hat{\psi}^\dagger(x_i) \, M_2(x_i, x_j) \, \hat{\psi}(x_i) \hat{\psi}(x_j)$$

$$= \frac{1}{2} \int dx \; dx' \; \hat{\psi}^\dagger(x') \; \hat{\psi}^\dagger(x) \;\; M_2(x, x') \;\; \hat{\psi}(x) \; \hat{\psi}(x')$$

result independent of N

expand in complete orthonormal set of orbitals

$$\hat{M}_2 = \frac{1}{2} \sum_{n,n',m,m'} \int dx dx' \, \overline{\varphi_{\alpha_{n'}}(x') \varphi_{\alpha_n}(x)} \, M_2(x, x') \, \varphi_{\alpha_m}(x) \varphi_{\alpha_{m'}}(x') \; c^\dagger_{\alpha_{n'}} c^\dagger_{\alpha_n} c_{\alpha_m} c_{\alpha_{m'}}$$

$$= \frac{1}{2} \sum_{n,n',m,m'} \langle \alpha_n \alpha_{n'} | M_2 | \alpha_m \alpha_{m'} \rangle \; c^\dagger_{\alpha_{n'}} c^\dagger_{\alpha_n} c_{\alpha_m} c_{\alpha_{m'}}$$

BO Hamiltonian

electronic Hamiltonian in Born-Oppenheimer approximation

$$H = -\frac{1}{2}\sum_{j=1}^{N_e}\nabla_j^2 - \sum_{j=1}^{N_e}\sum_{\alpha=1}^{N_i}\frac{Z_\alpha}{|r_j - R_\alpha|} + \sum_{j<k}^{N_e}\frac{1}{|r_j - r_k|} + \sum_{\alpha<\beta}^{N_i}\frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}$$

solve $H\Psi(\boldsymbol{x}_1, ..., \boldsymbol{x}_N) = E\Psi(\boldsymbol{x}_1, ..., \boldsymbol{x}_N)$ and antisymmetrize

solve $H|N_e\rangle = E|N_e\rangle$, where

$$H = -\sum_{\alpha\beta} t_{\alpha\beta}\, c_\alpha^\dagger c_\beta + \frac{1}{2}\sum_{\alpha\beta\gamma\delta} U_{\substack{\alpha\delta\\ \beta\gamma}}\, c_\alpha^\dagger c_\beta^\dagger c_\gamma c_\delta \qquad |N_e\rangle = \sum a_{\alpha_1,\ldots,\alpha_{Ne}} \prod_i c_{\alpha_i}^\dagger |0\rangle$$

$$t_{\alpha\beta} = \sum_{\alpha'\beta'} (S^{-1})_{\alpha\alpha'} \int dx\, \overline{\varphi_{\alpha'}(x)} \left(\frac{1}{2}\vec{\nabla}^2 - V_{\text{ext}}(\vec{r})\right) \varphi_{\beta'}(x)\ \ (S^{-1})_{\beta'\beta}$$

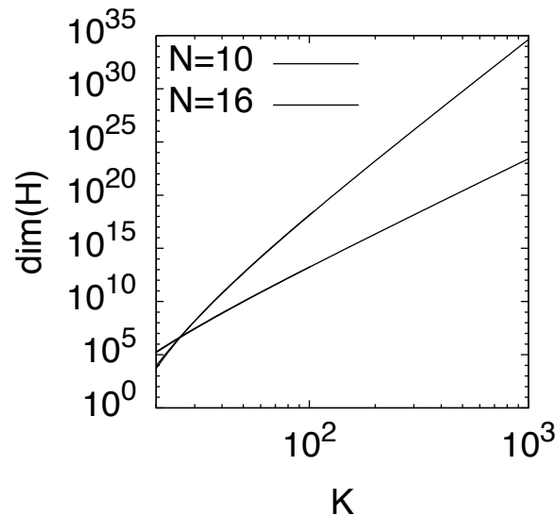
$$U_{\substack{\alpha\delta\\ \beta\gamma}} = \sum_{\substack{\alpha'\delta'\\ \beta'\gamma'}} S^{-1}_{\alpha\alpha'}\, S^{-1}_{\beta\beta'} \int dx \int dx'\, \overline{\varphi_{\alpha'}(x)}\, \overline{\varphi_{\beta'}(x')}\, \frac{1}{|\vec{r} - \vec{r}\,'|}\, \varphi_{\gamma'}(x')\varphi_{\delta'}(x)\, S^{-1}_{\gamma'\gamma}\, S^{-1}_{\delta'\delta}$$

approximation: restrict basis set

formulations in 1st and 2nd quantization equivalent,
as long as basis set complete

restrict basis set to K functions φ_α

N-electron Hilbert space restricted to
binom(K,N)-dimensional *variational* space



all-electron approach:
increase K until convergence

pseudized approach:
variational space only for *interesting* electrons

how?
perturbation theory
renormalization

perturbation theory: atomic multiplets

$$H = \sum_j \left(-\frac{1}{2}\nabla_j^2 - \frac{Z}{r_j} \right) + \sum_{k<j} \frac{1}{|r_j - r_k|}$$

$$= \underbrace{\sum_j \left(-\frac{1}{2}\nabla_j^2 - \frac{Z}{r_j} + U_{\mathrm{scf}}(r_j) \right)}_{=:H_0} + \underbrace{\sum_j \left(\sum_{k<j} \frac{1}{|r_j - r_k|} - U_{\mathrm{scf}}(r_j) \right)}_{=:H_1}$$

H_1 should be small perturbation

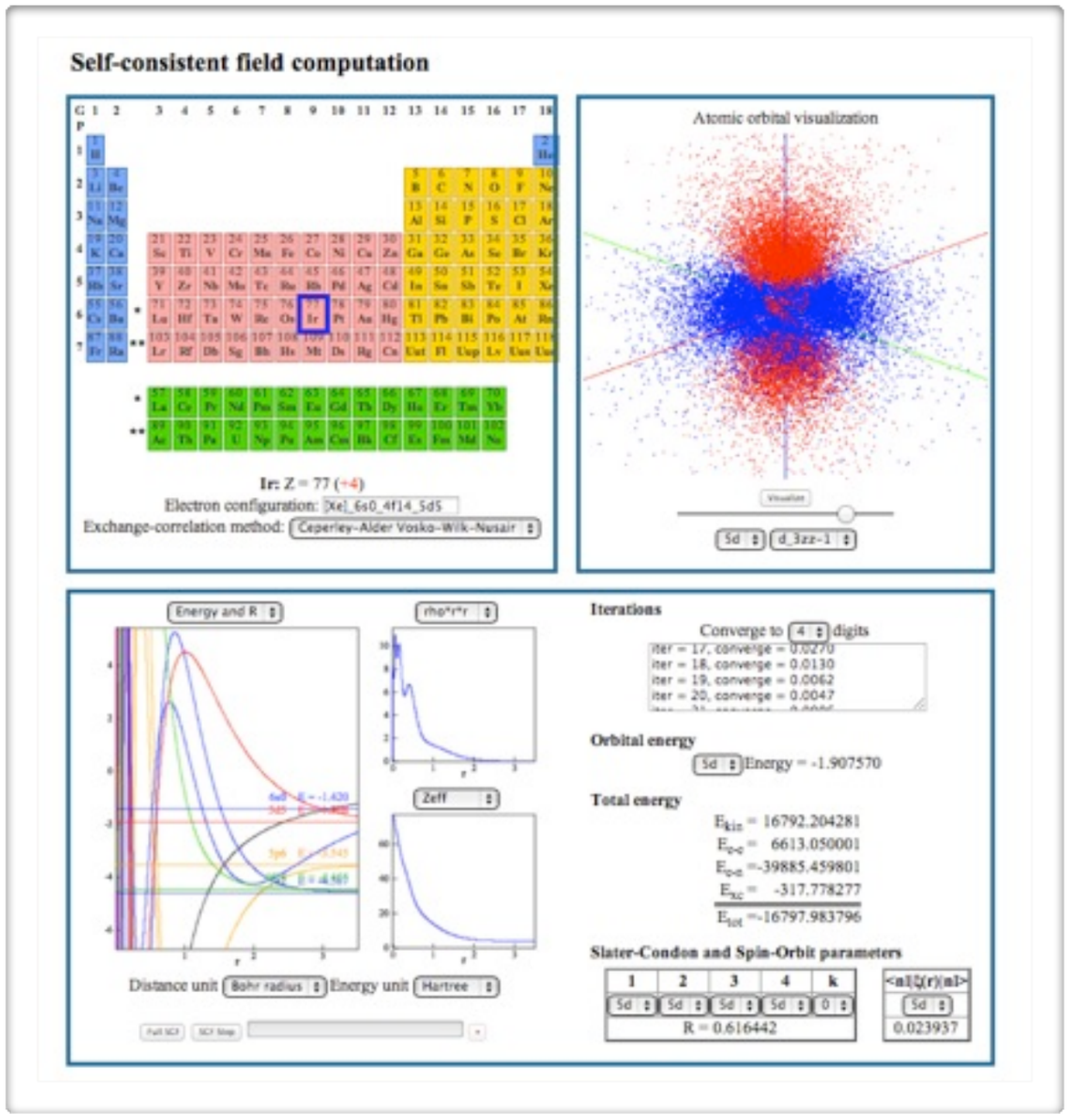
U_{scf} must describe electron-electron repulsion well

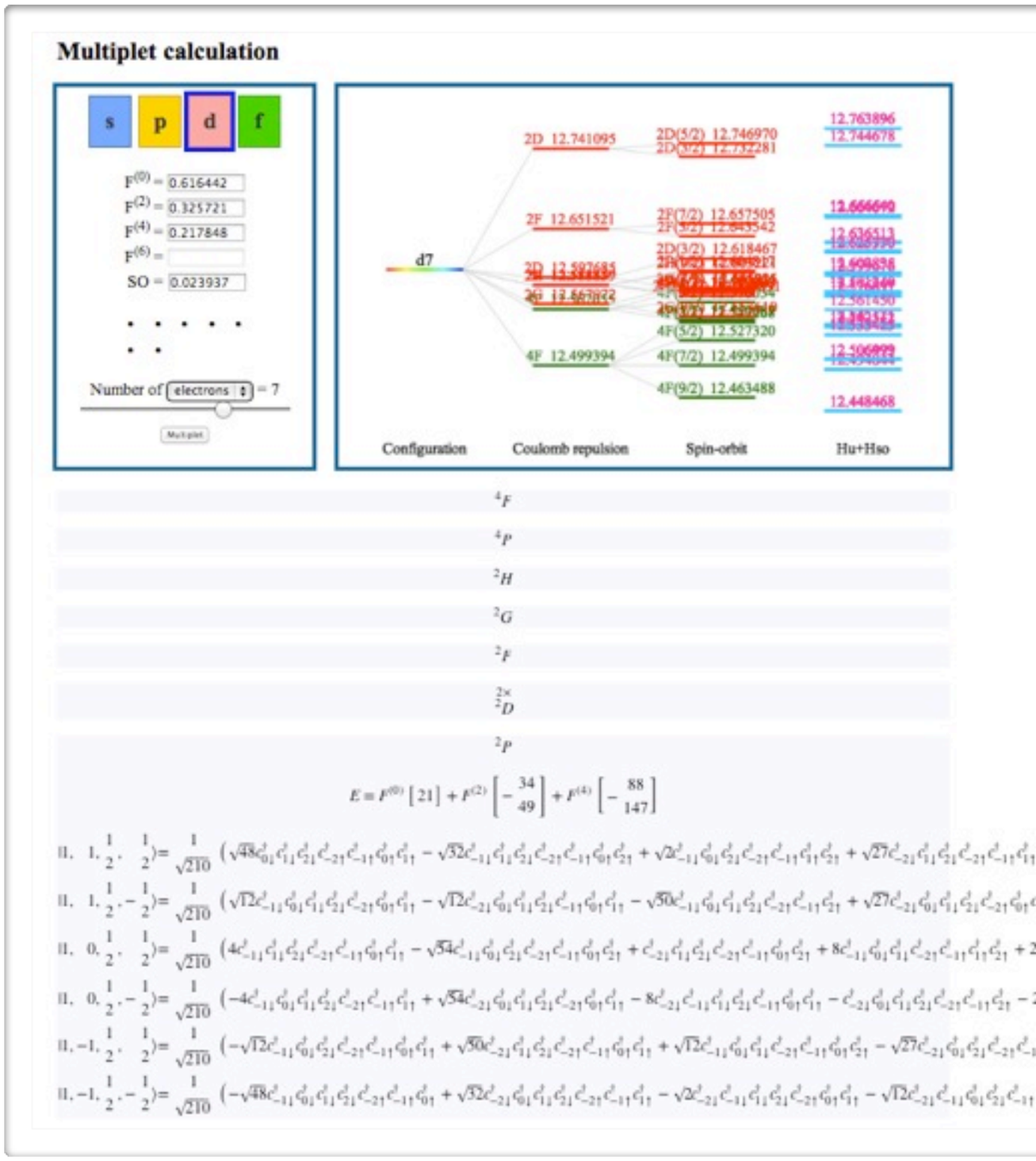
accurate density gives accurate Hartree term

DFT orbitals!

open shell − degenerate perturbation theory

atomic multiplets





Q. Zhang:
Calculations of Atomic Multiplets across the Periodic Table
MSc thesis, RWTH Aachen 2014
www.cond-mat.de/sims/multiplet

Hund's rule: d^5 ground state ^6S

$$|0,0,5/2,\ \ 5/2\rangle = c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\,|0\rangle$$

$$|0,0,5/2,\ \ 3/2\rangle = \frac{1}{\sqrt{5}}\left(c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{0\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\right)|0\rangle$$

$$\begin{aligned}|0,0,5/2,\ \ 1/2\rangle = \frac{1}{\sqrt{10}}\Big(&c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow} - c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow} + c^\dagger_{-1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} + c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow}c^\dagger_{2\uparrow}\\ &-c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\Big)|0\rangle\end{aligned}$$

$$\begin{aligned}|0,0,5/2,-1/2\rangle = \frac{1}{\sqrt{10}}\Big(&c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{-1\uparrow} - c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{0\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{0\uparrow} + c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{1\uparrow}\\ &+c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{0\uparrow}c^\dagger_{1\uparrow} - c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-2\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{-1\uparrow}c^\dagger_{2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{0\uparrow}c^\dagger_{2\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\uparrow}c^\dagger_{2\uparrow}\Big)|0\rangle\end{aligned}$$

$$|0,0,5/2,-3/2\rangle = \frac{1}{\sqrt{5}}\left(c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-2\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{-1\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}c^\dagger_{0\uparrow} - c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{2\downarrow}c^\dagger_{1\uparrow} + c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\uparrow}\right)|0\rangle$$

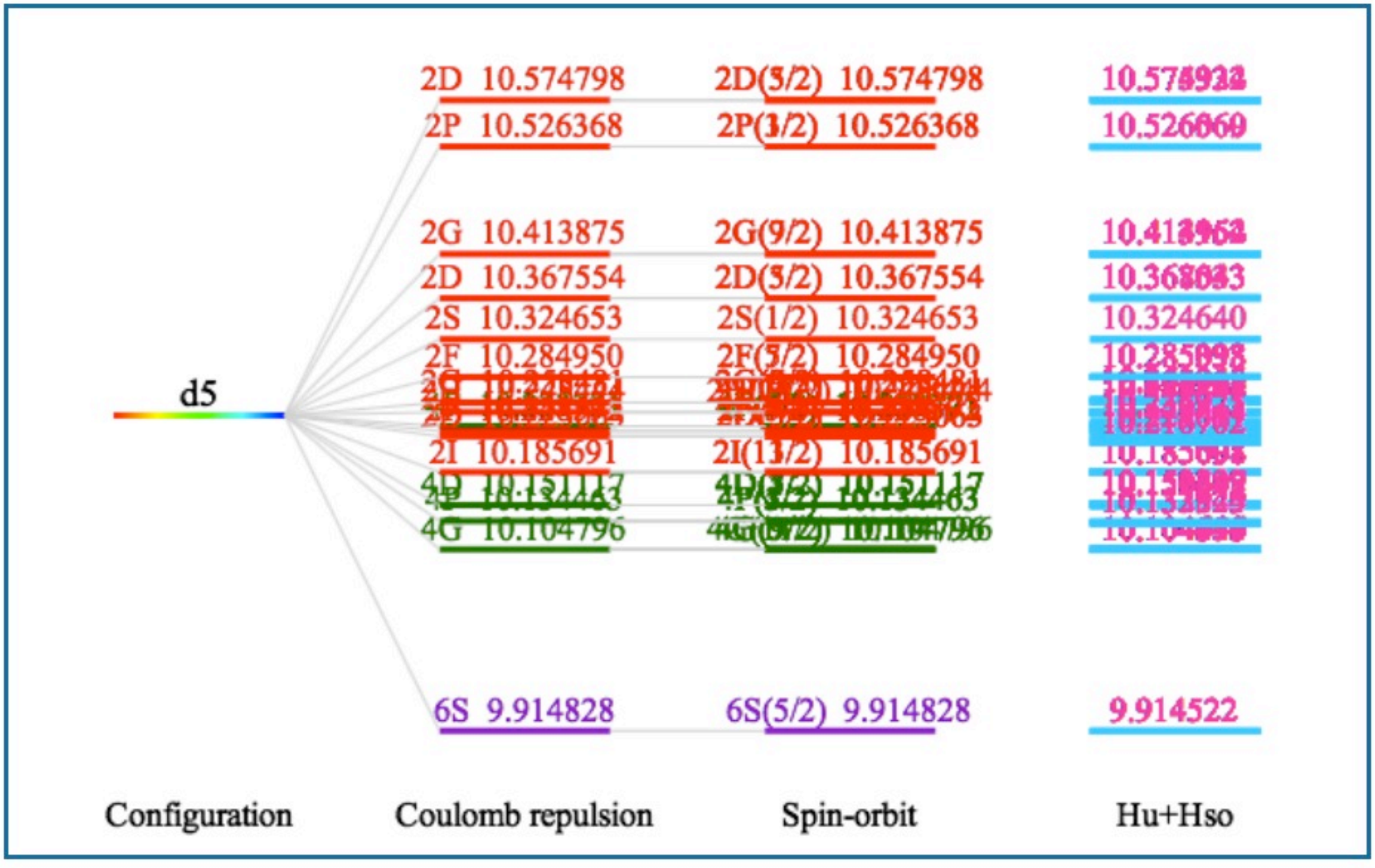
$$|0,0,5/2,-5/2\rangle = c^\dagger_{-2\downarrow}c^\dagger_{-1\downarrow}c^\dagger_{0\downarrow}c^\dagger_{1\downarrow}c^\dagger_{2\downarrow}\,|0\rangle$$

$$E_{^6S} = 10\,F^{(0)} - \frac{5}{7}\left(F^{(2)} + F^{(4)}\right)$$

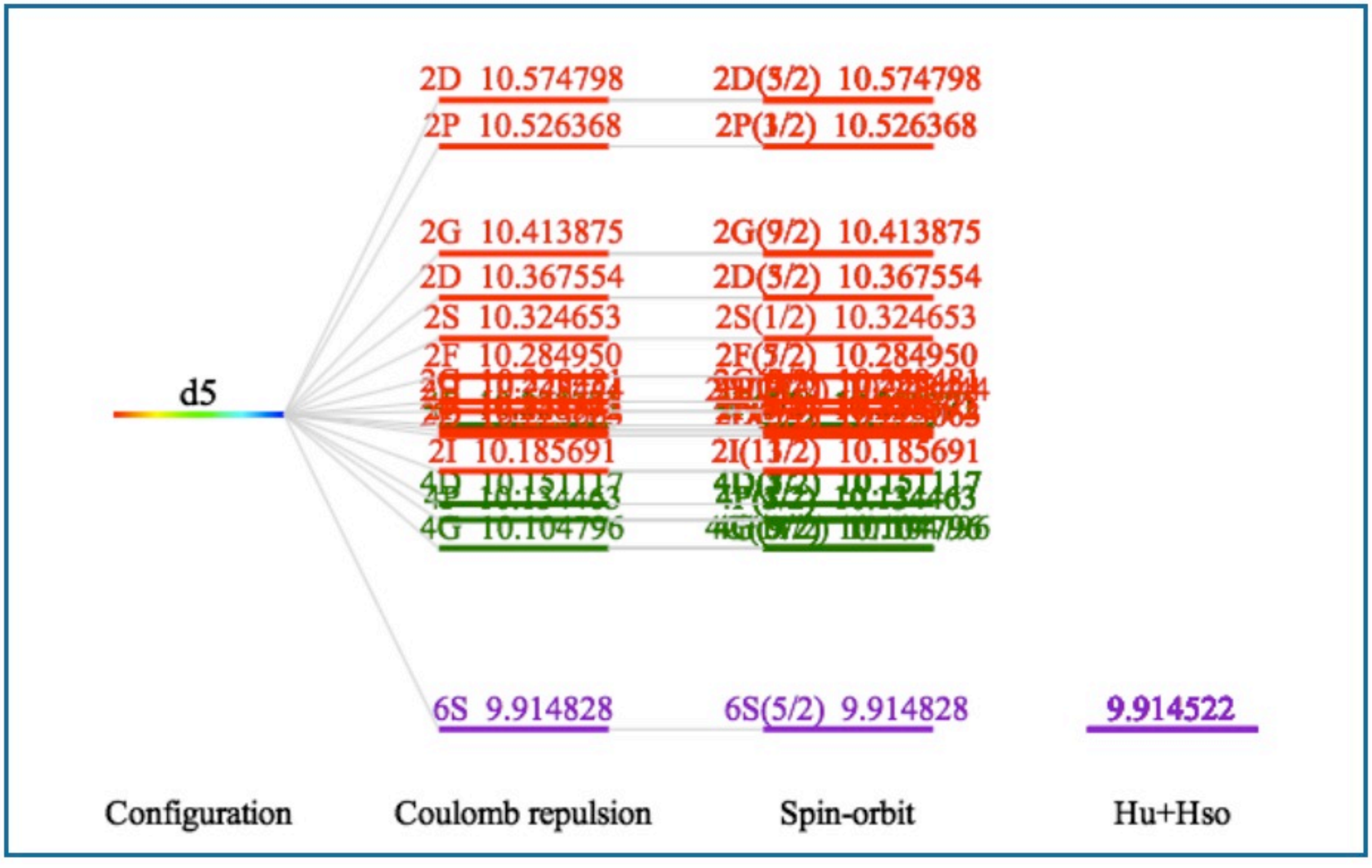
Slater integrals $$F^{(k)}_{nl} = \int_0^\infty dr\,|u_{nl}(r)|^2\left(\frac{1}{r^{k+1}}\int_0^r d\tilde{r}\,\tilde{r}^k\,|u_{nl}(\tilde{r})|^2 + r^k\int_r^\infty d\tilde{r}\,\frac{1}{\tilde{r}^{k+1}}\,|u_{nl}(\tilde{r})|^2\right)$$

Spin-Orbit coupling $$H_{SO} = \frac{1}{2c^2}\sum_i \frac{1}{r_i}\frac{dV}{dr_i}\,\ell_i\cdot\mathbf{s}_i$$

LS coupling: Co^{4+}

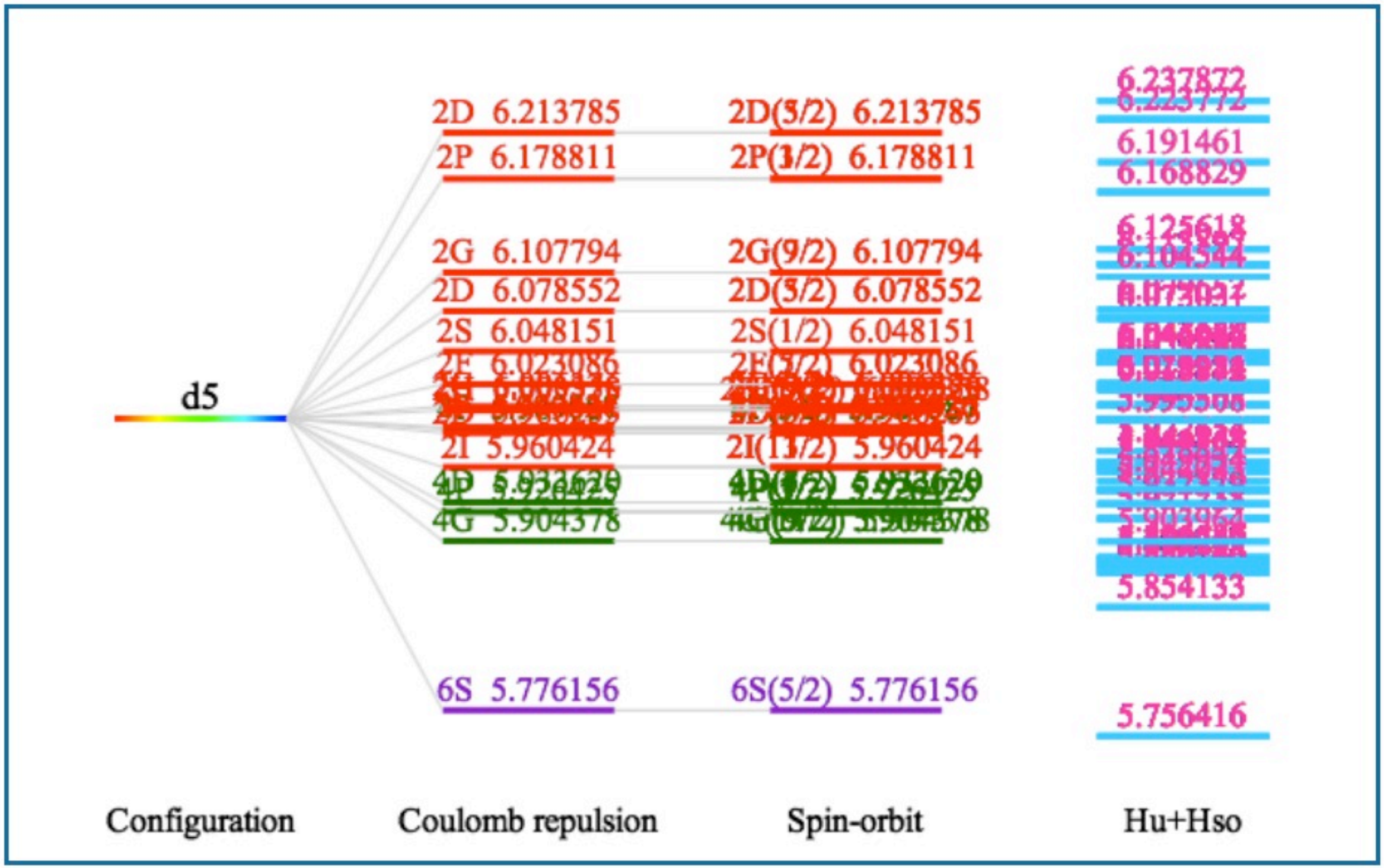


LS coupling: Co^{4+}

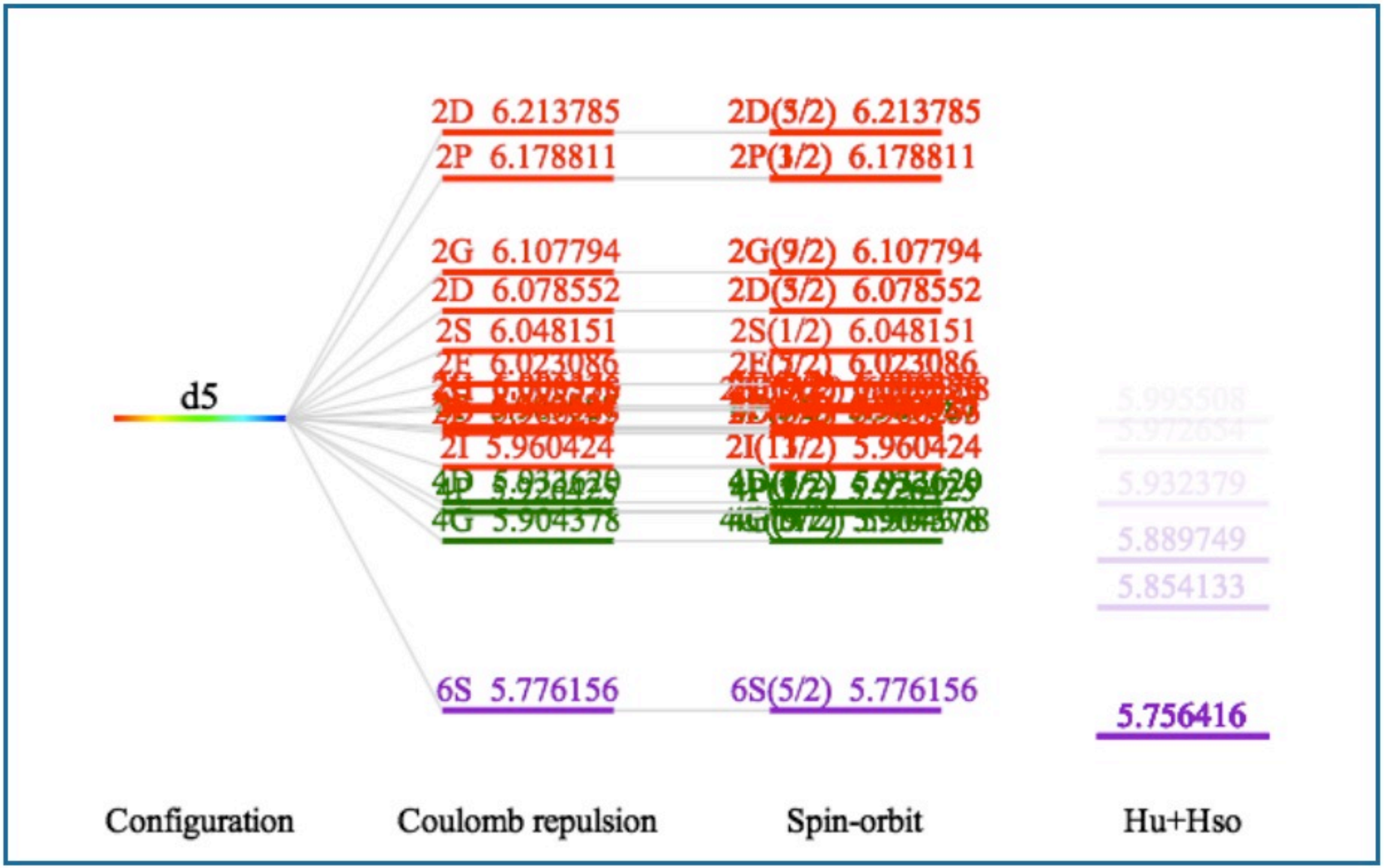


^6S character

non-LS coupling: Ir^{4+}

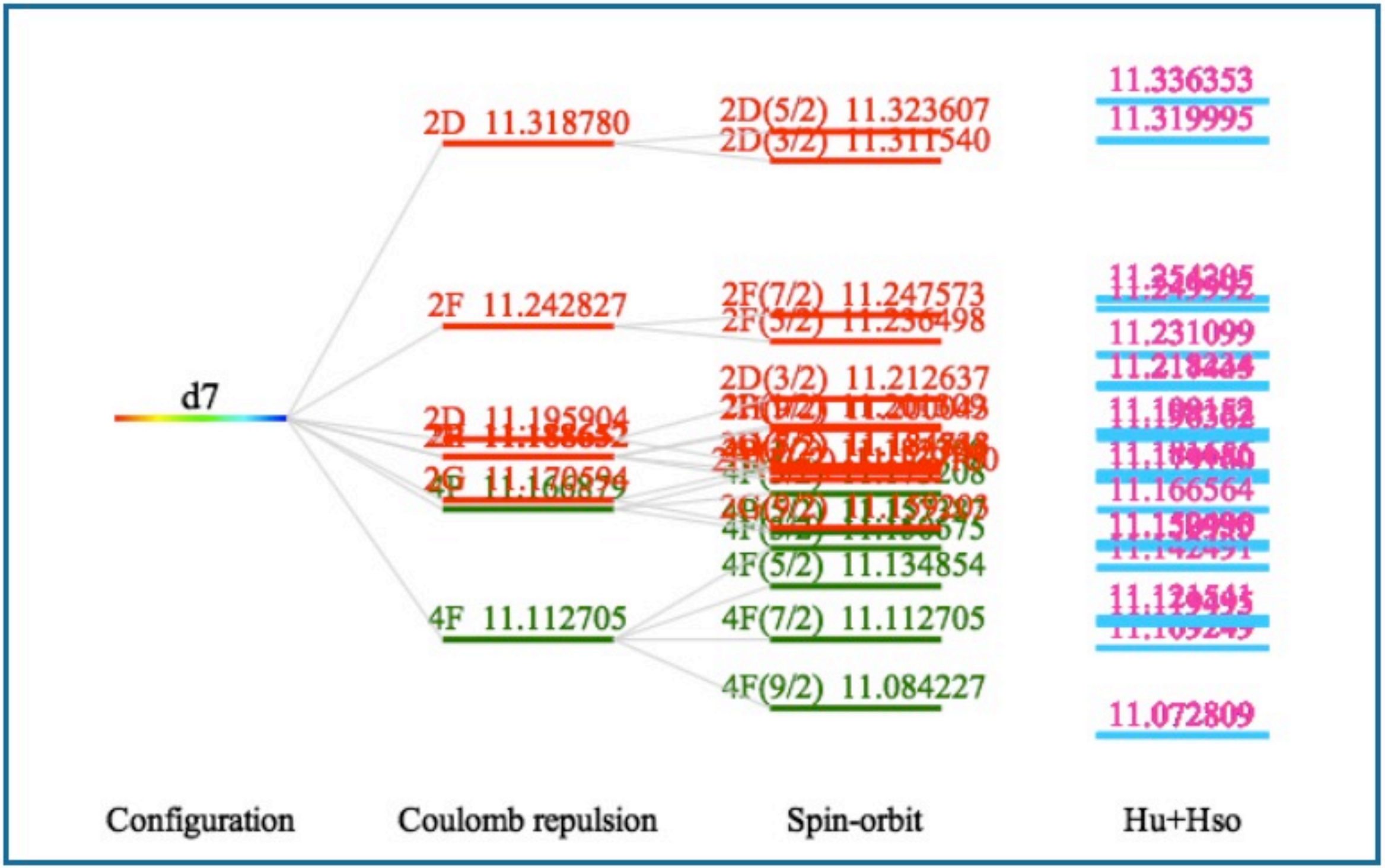


non-LS coupling: Ir^{4+}



^6S character

non-LS coupling: Ir atom



modeling correlated electrons: renormalization

$$H = -\frac{1}{2}\sum_{j=1}^{N_e}\nabla_j^2 - \sum_{j=1}^{N_e}\sum_{\alpha=1}^{N_i}\frac{Z_\alpha}{|r_j - R_\alpha|} + \sum_{j<k}^{N_e}\frac{1}{|r_j - r_k|}$$

complete orbital basis $\varphi_{n,i}$ $\quad H = -\sum_{n,i;m,j;\sigma} t_{n,i;m,j}\, a^\dagger_{m,j\sigma}\, a_{n,i\sigma} + \sum_i V_{n,i\sigma;m,j\sigma'}\, n_{n,i\sigma}\, n_{m,j\sigma'}$

distinguish **two types of electrons/orbitals**: correlated and uncorrelated

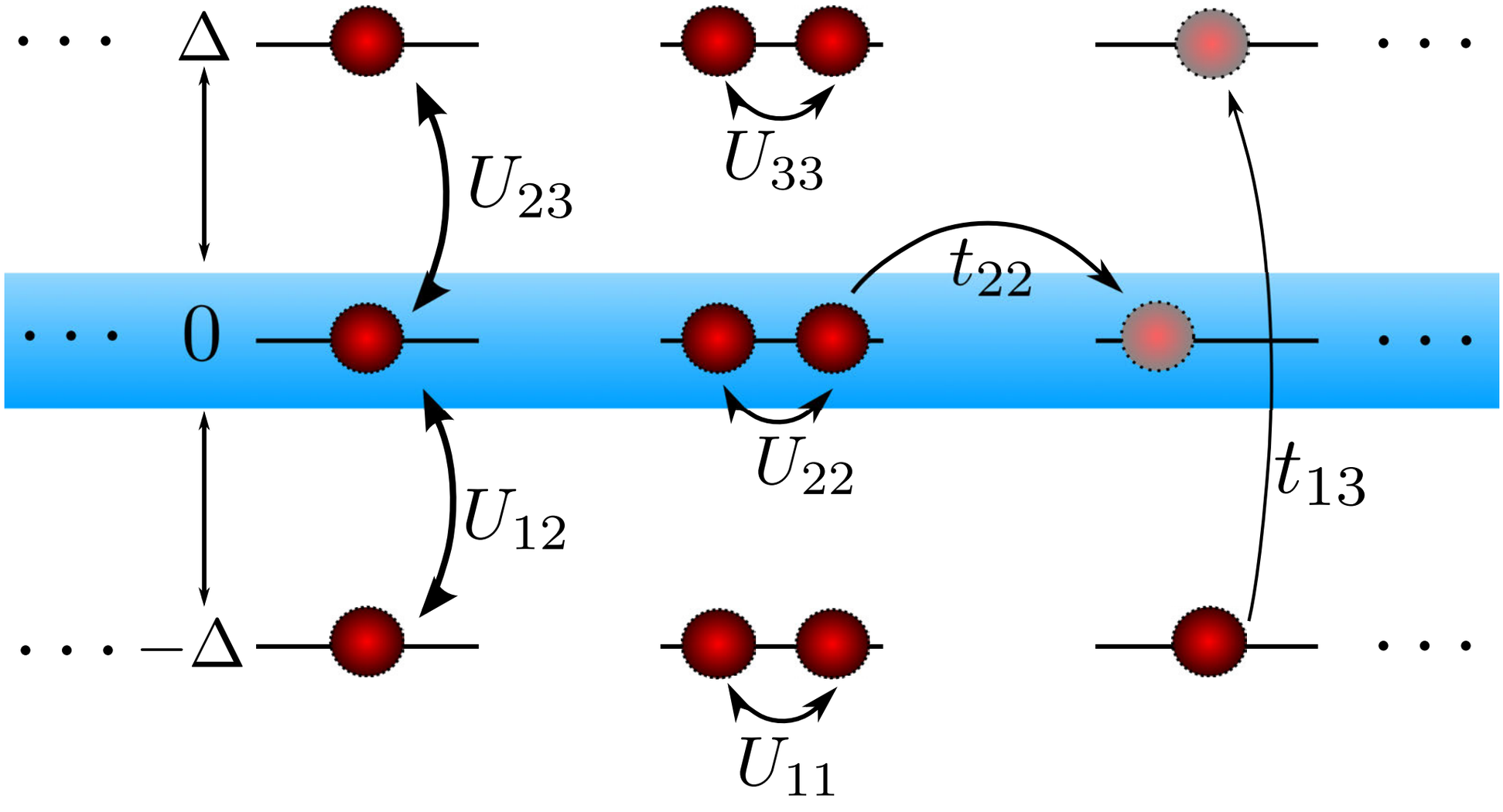
assume no hybridization between them: product ansatz

$$\Psi(\{n_{n,i\sigma}\}) = \sum_n \sum_\mu \alpha_{i,\mu}\psi_n(\{n_{c,i\sigma}\})\,\Phi_\mu(\{n_{c,i\sigma}\};\{n_{a,j\sigma'}\}) \approx \psi_0\,\Phi(\{n_{c,i\sigma}\})$$

instant-screening approx.: **slow** correlated, fast other electrons

$$H|\Psi\rangle = E|\Psi\rangle \;\Rightarrow\; \langle\Phi|H|\Phi\rangle|\psi\rangle = E|\psi\rangle$$

simple example: 3-band Hubbard cluster



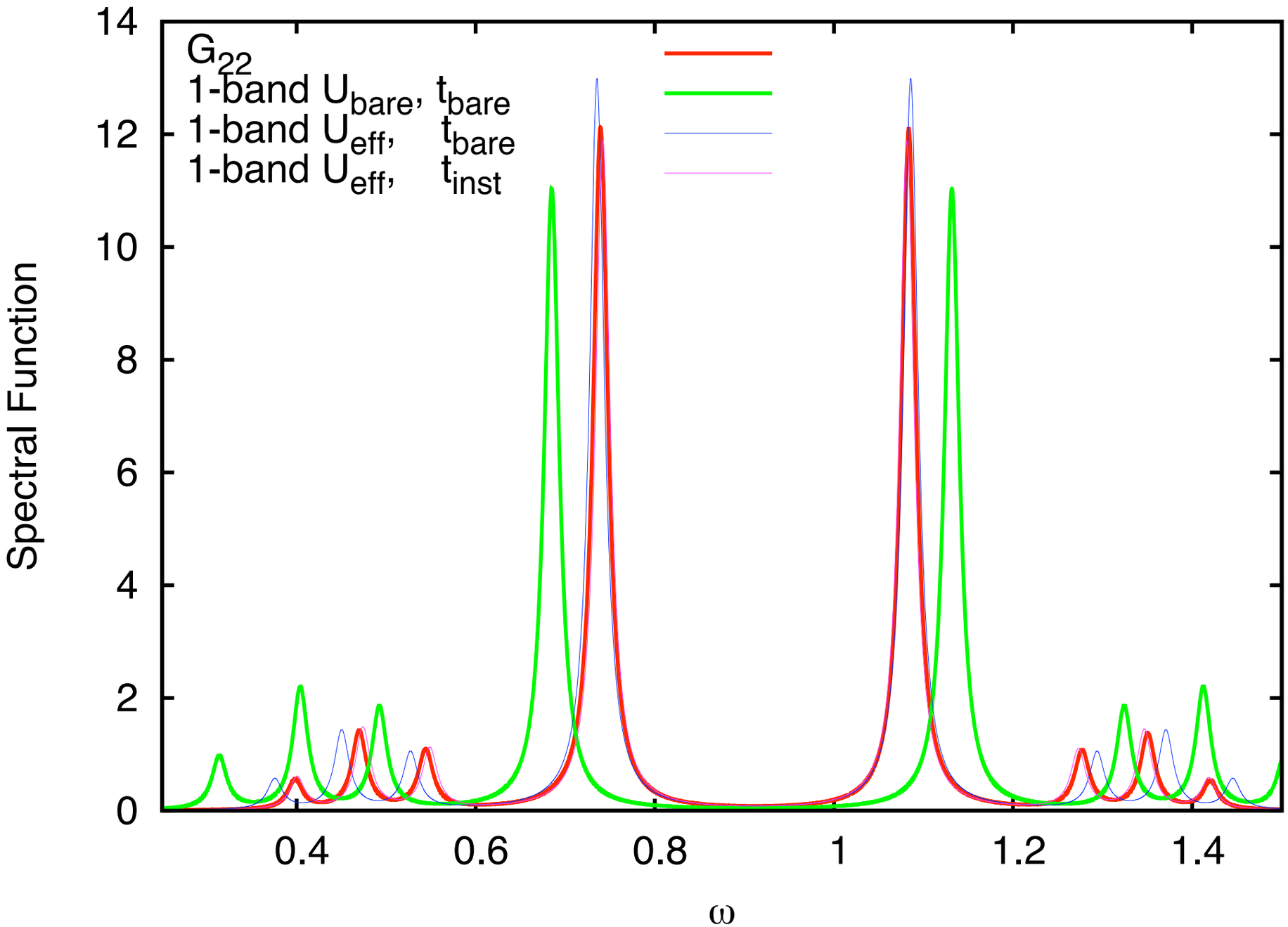
U_{11} = 1.5
U_{22} = 0.6
U_{33} = .2

U_{12} = 0.7
U_{23} = 0.05

t_{22} = 0.1
t_{13} = 0.5

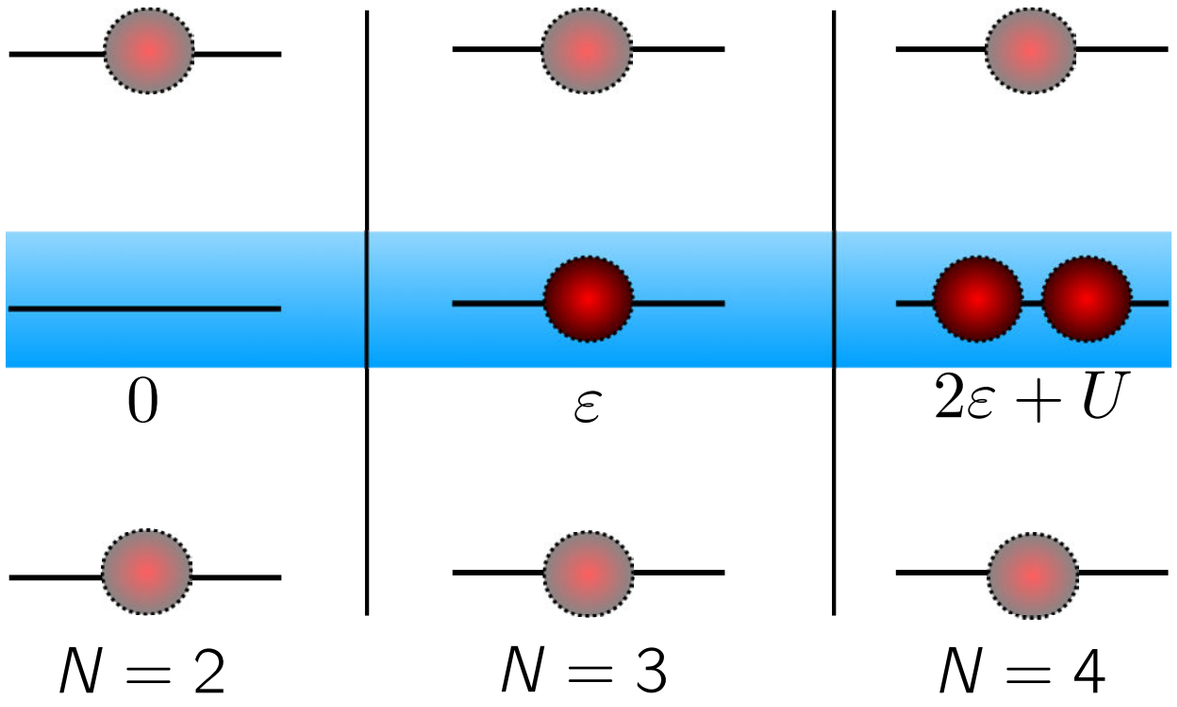
Δ = 0.5

spectral function: projected vs. 1-band

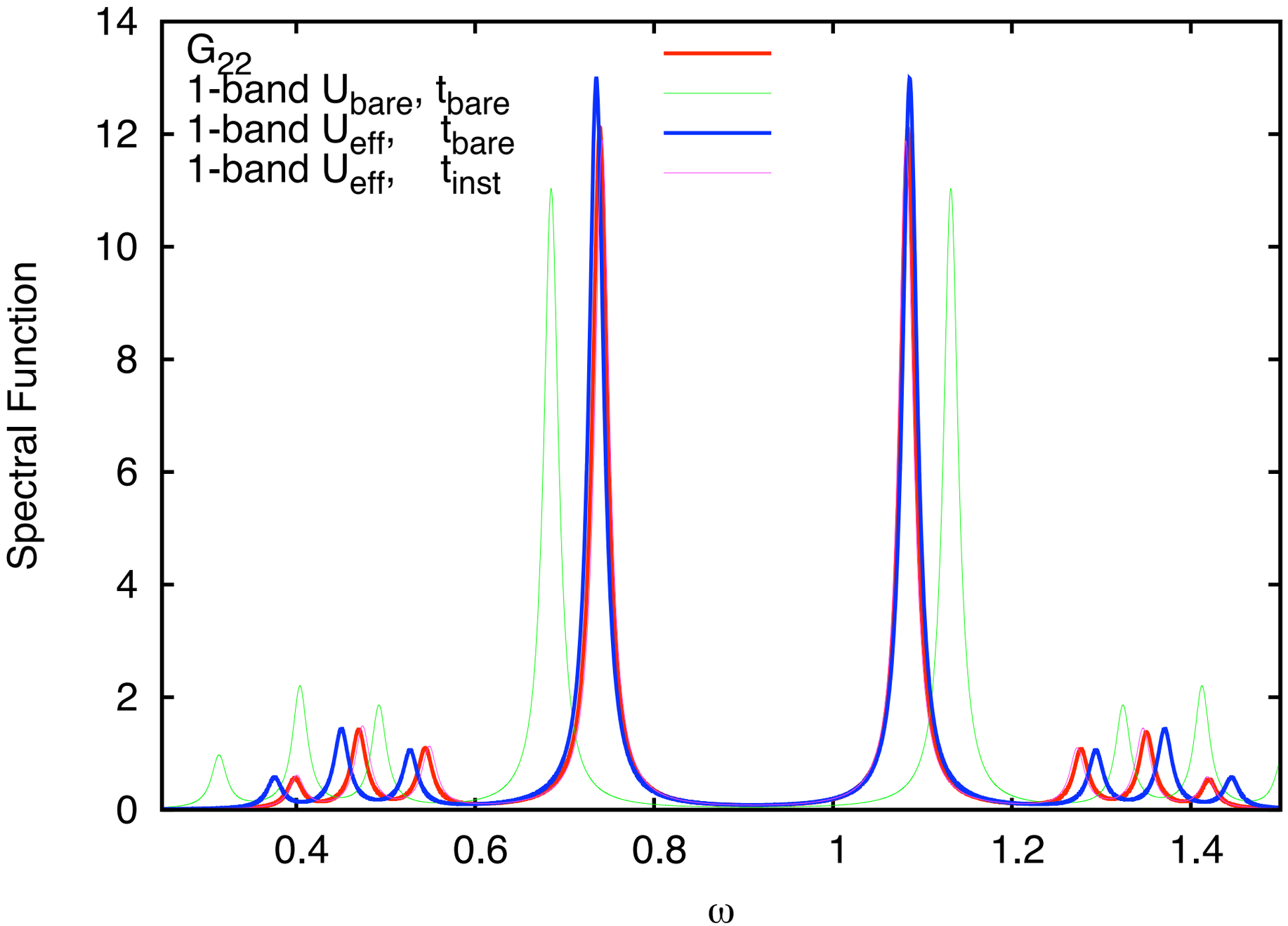


screening *U*

instantaneous screening approximation

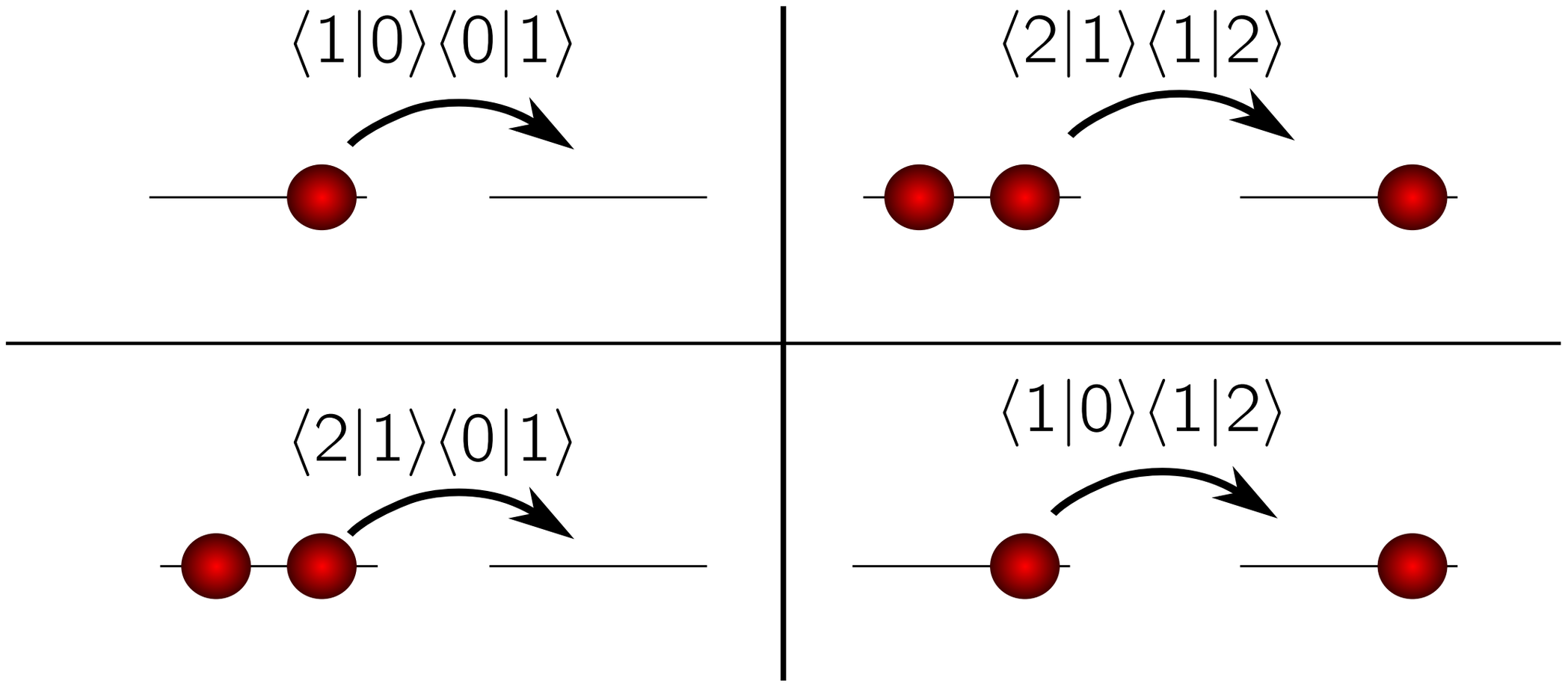


spectral function: projected vs. 1-band

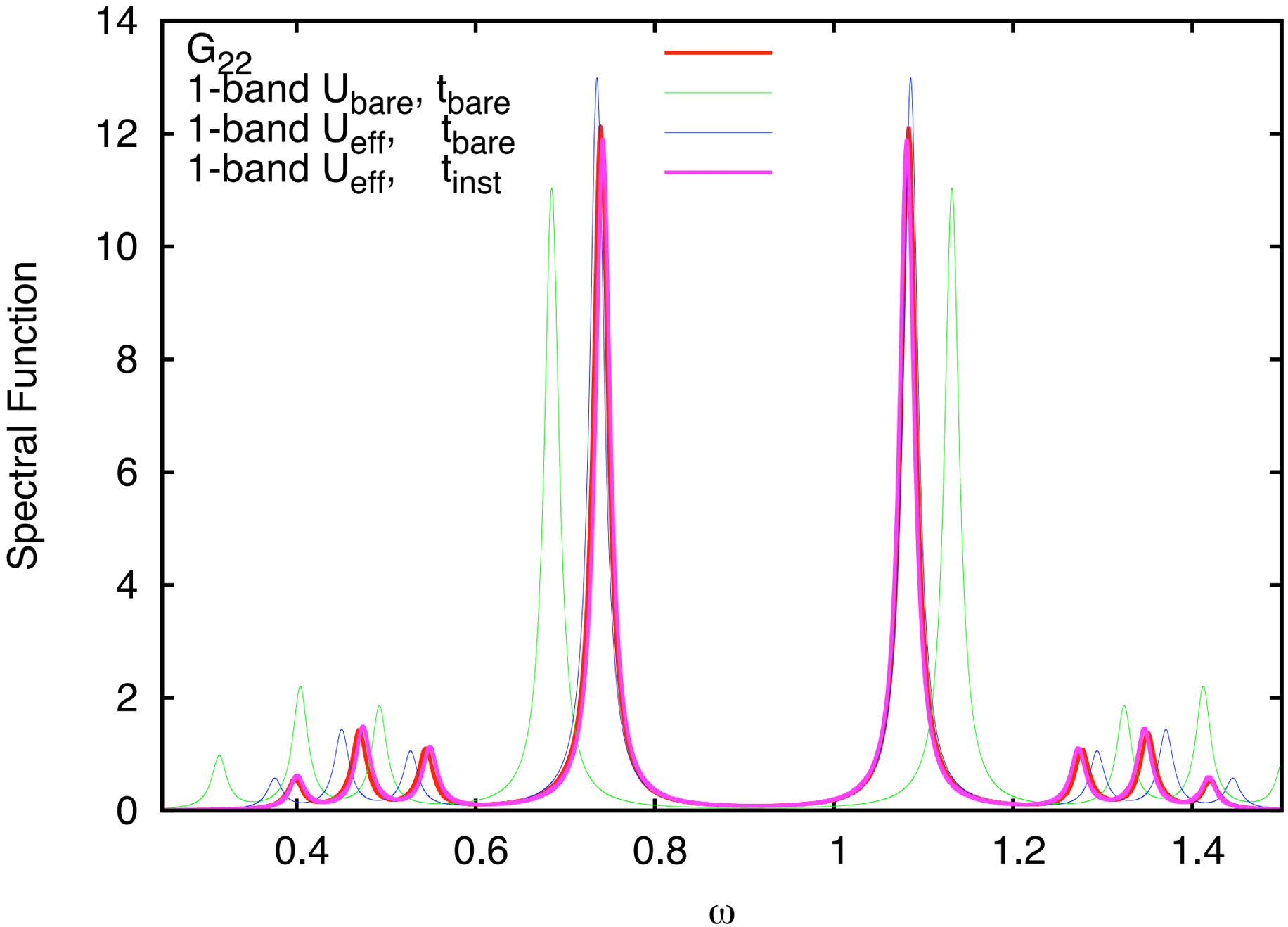


hopping reduction

overlap between different screening states reduces hopping: t_{eff}



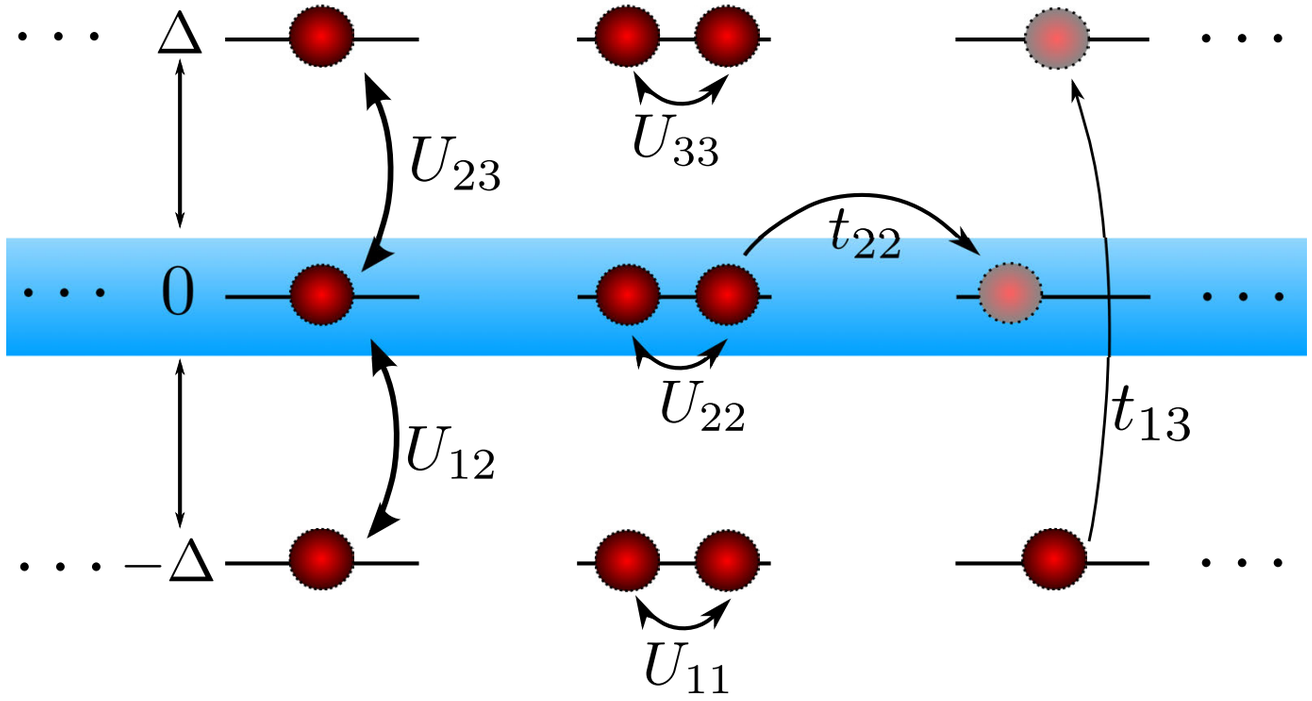
spectral function: projected vs. 1-band



screening reduces *U* and *t*

could justify that constrained calculations tend to give “too small *U*”

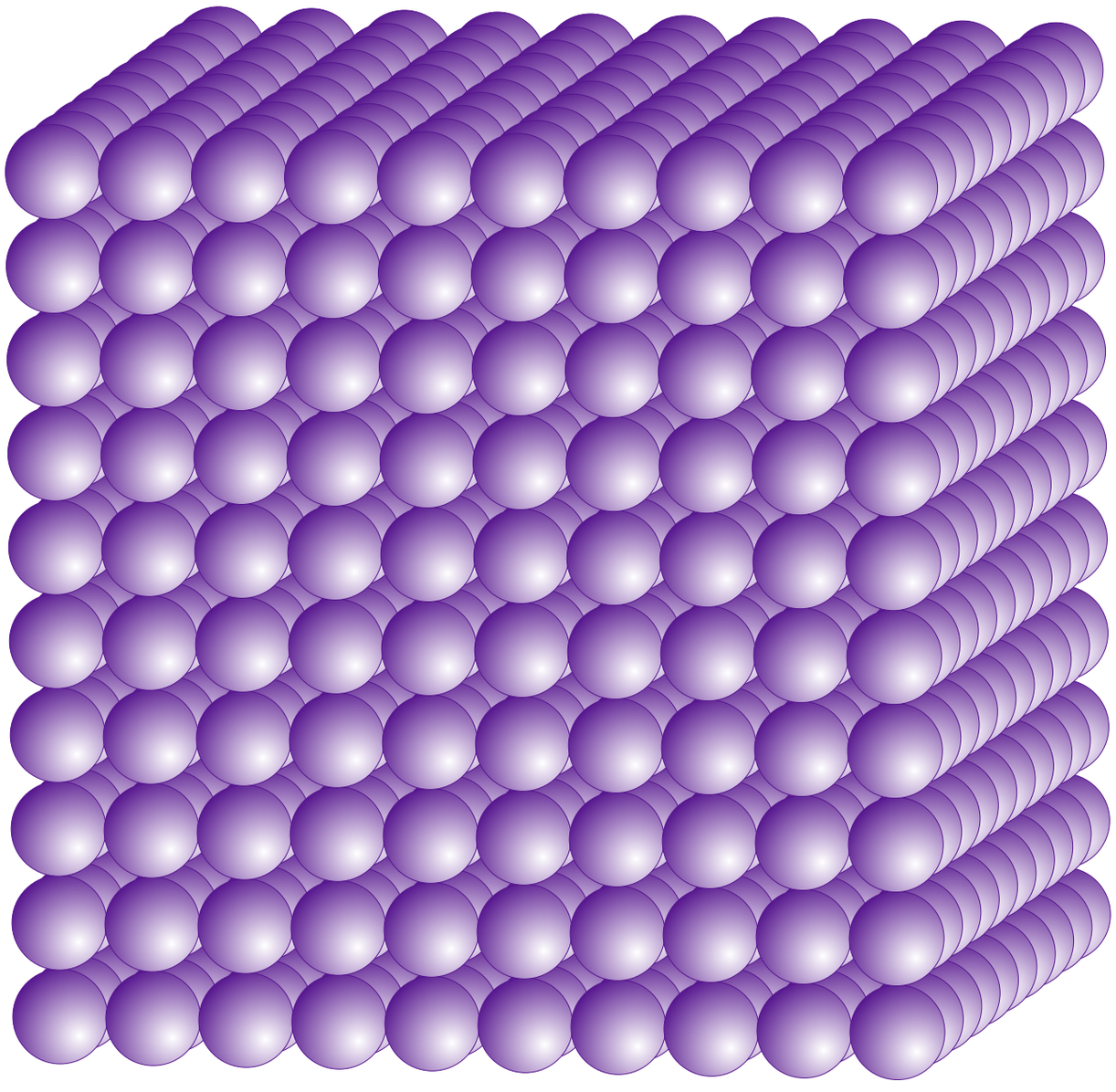
t/U not as sensitive to screening as one might think



C. Adolphs:
Renormalization of the Coulomb Interaction in the Hubbard Model
Diploma Thesis, RWTH Aachen 2010

surface effects

10×10×10 cluster



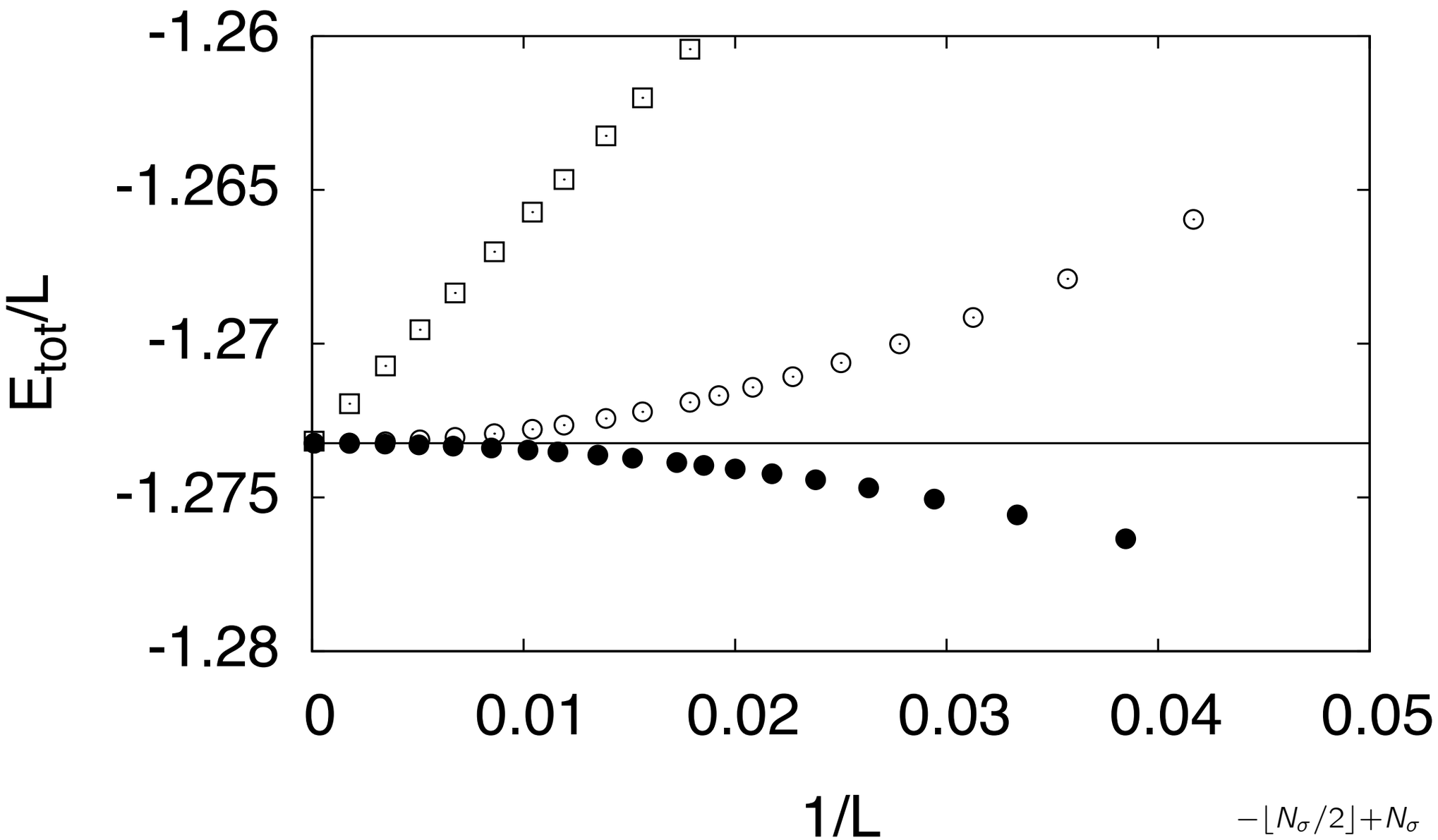
$8^3=2^9=512$ atoms inside

almost 50% of atoms
on surface...

how to simulate bulk?

periodic boundary conditions

finite size scaling



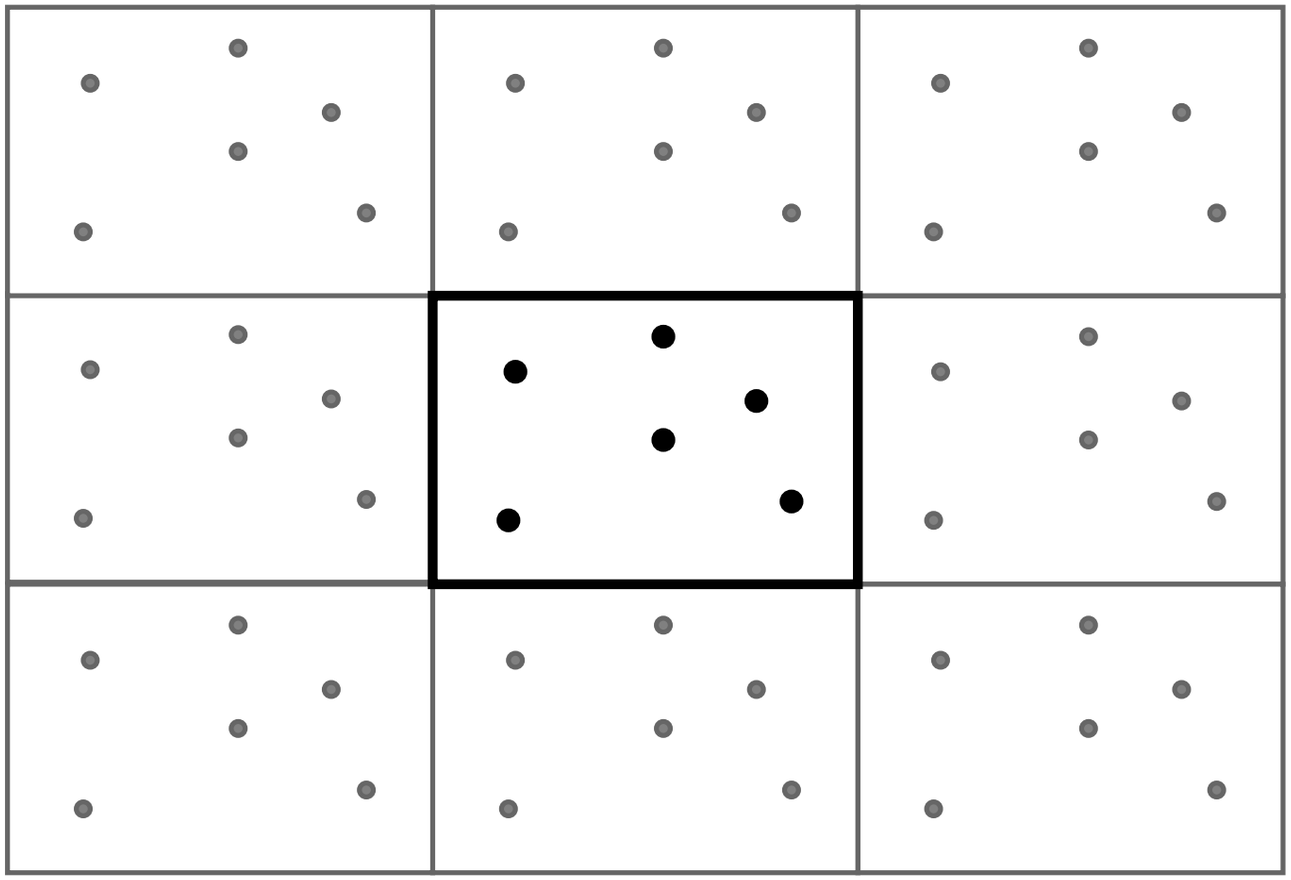
half-filled one-dimensional L-site chain

$$E_{\mathrm{pbc}} = -2t \sum_{\sigma} \sum_{n=-\lfloor N_\sigma/2 \rfloor}^{-\lfloor N_\sigma/2 \rfloor + N_\sigma} \cos(2\pi n/L)$$

$$E_{\mathrm{obc}} = -2t \sum_{\sigma} \sum_{n=1}^{N_\sigma} \cos(2\pi n/(L+1))$$

periodic boundary conditions

additional interaction with periodic images



$$H_{\text{pbc}} = -\frac{1}{2}\sum_{i=1}^{N}\vec{\nabla}_i^2 + \sum_{\vec{n}\in\mathbb{Z}^3}\sum_{i} V_{\text{ext}}^{\mathcal{C}}(\vec{r}_i - \vec{R}_{\vec{n}}) + \frac{1}{2}\sum_{\vec{n}\in\mathbb{Z}^3}{\sum_{i,j}}' \frac{1}{|\vec{r}_i - \vec{r}_j - \vec{R}_{\vec{n}}|}$$

finite-size correction $\quad \varepsilon = \big(E_{\text{corr}}(L) - E_{\text{MF}}(L)\big)/L + \varepsilon_{\text{MF}}$

exchange-correlation hole

electron density: $\Gamma(x; x) = n(x)$

conditional electron density: $2\Gamma(x, x'; x, x') = n(x, x')$

electron density at *x'* given that an electron is at *x*

Coulomb repulsion $\langle U \rangle = \int dx\, dx'\, \frac{\Gamma^{(2)}(x, x'; x, x')}{|r - r'|} = \frac{1}{2} \int dx\, dx' \frac{n(x, x')}{|r - r'|}$

rewrite in terms of Hartree energy

(how $\langle U \rangle$ differs from mean-field)

$$n(x, x') = n(x)n(x')\, g(x, x') = n(x)n(x') + n(x)n(x')\, (g(x, x') - 1)$$

pair correlation function

Hartree term

exchange-correlation hole

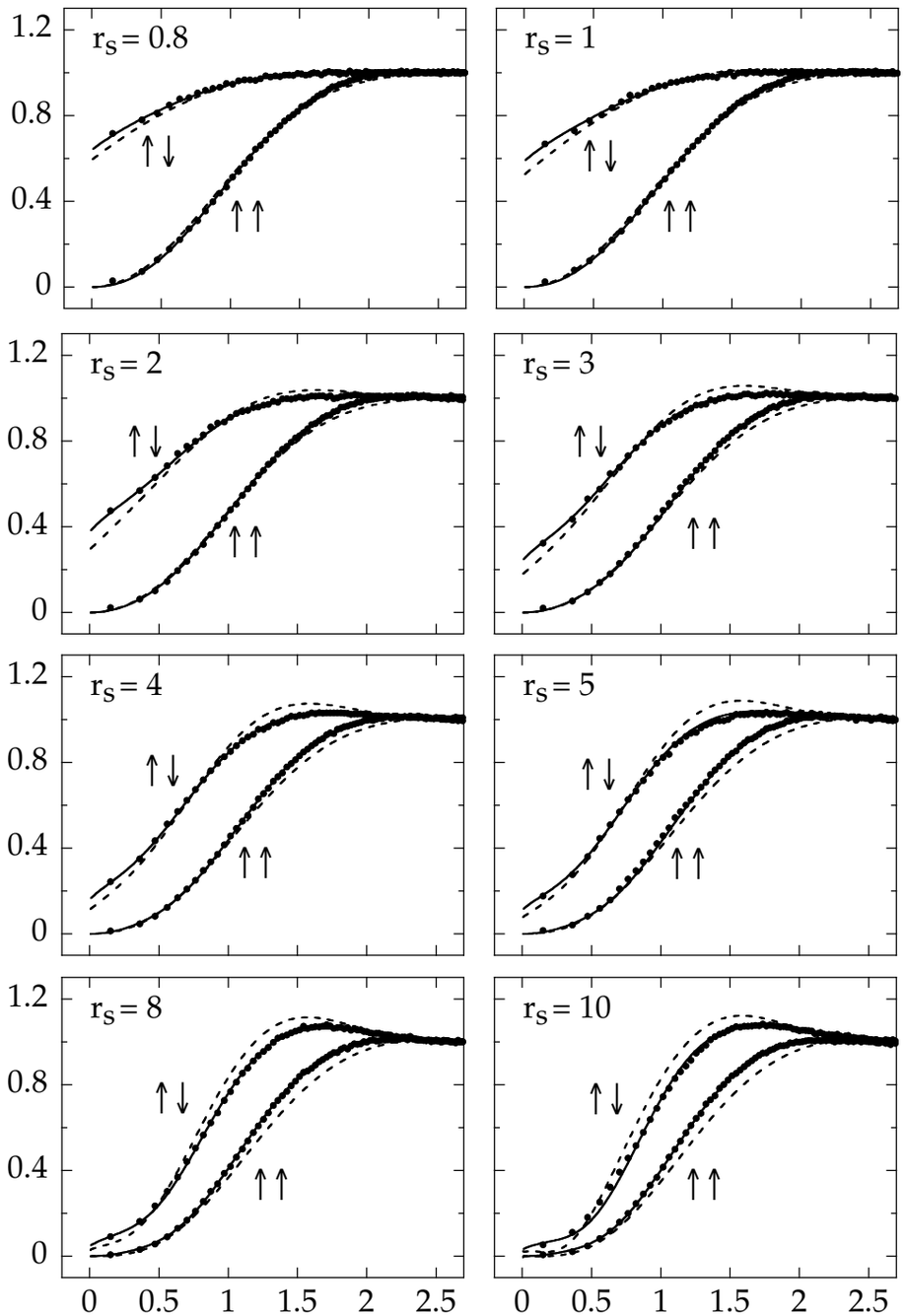
sum rule

$$\int dx'\, n(x, x') = n(x)\, (N - 1)$$

$$\int dx'\, n(x')\, \big(g(x, x') - 1\big) = -1$$

exchange-correlation holes from QMC

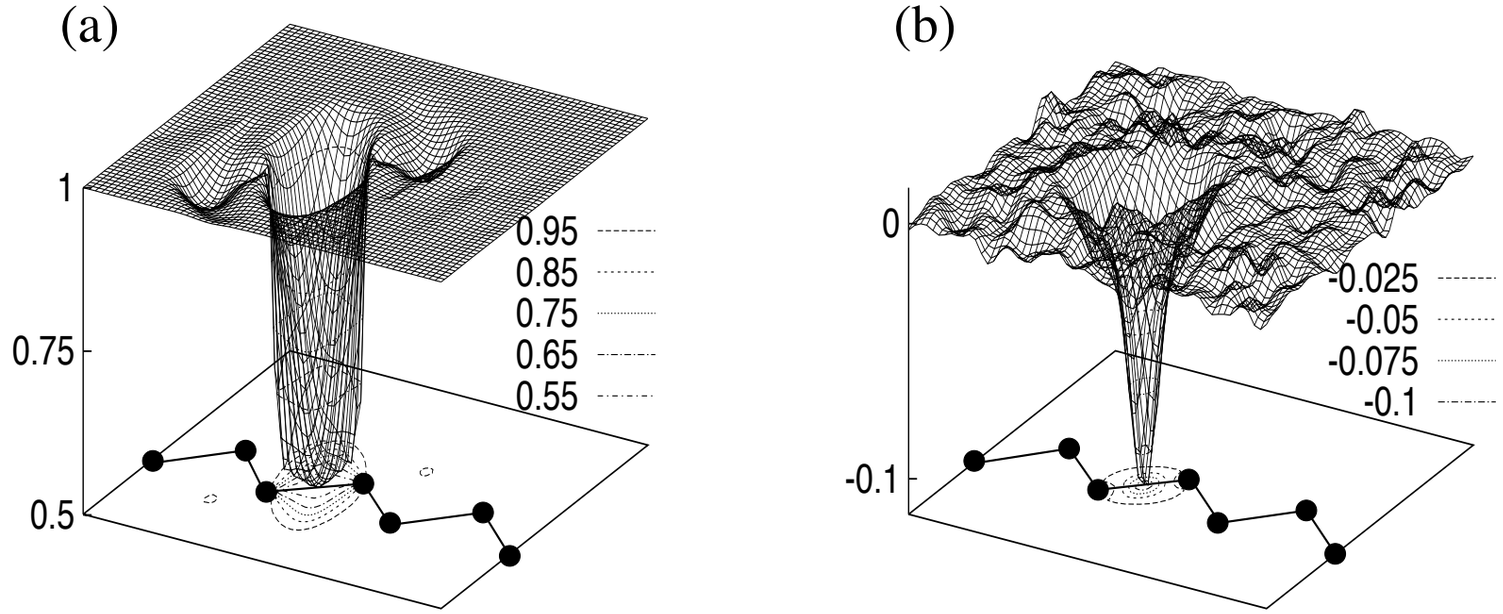
homogeneous electron gas $g_{xc}^{\sigma\sigma'}(r/r_s)$



G. Ortiz, M. Harris, P. Ballone, Phys. Rev. Lett. 82, 5317 (1999)
P. Gori-Giorgi, F. Sacchetti, G.B. Bachelet, Phys. Rev. B 61, 7353 (2000)

(110) plane of Si, electron at bond center

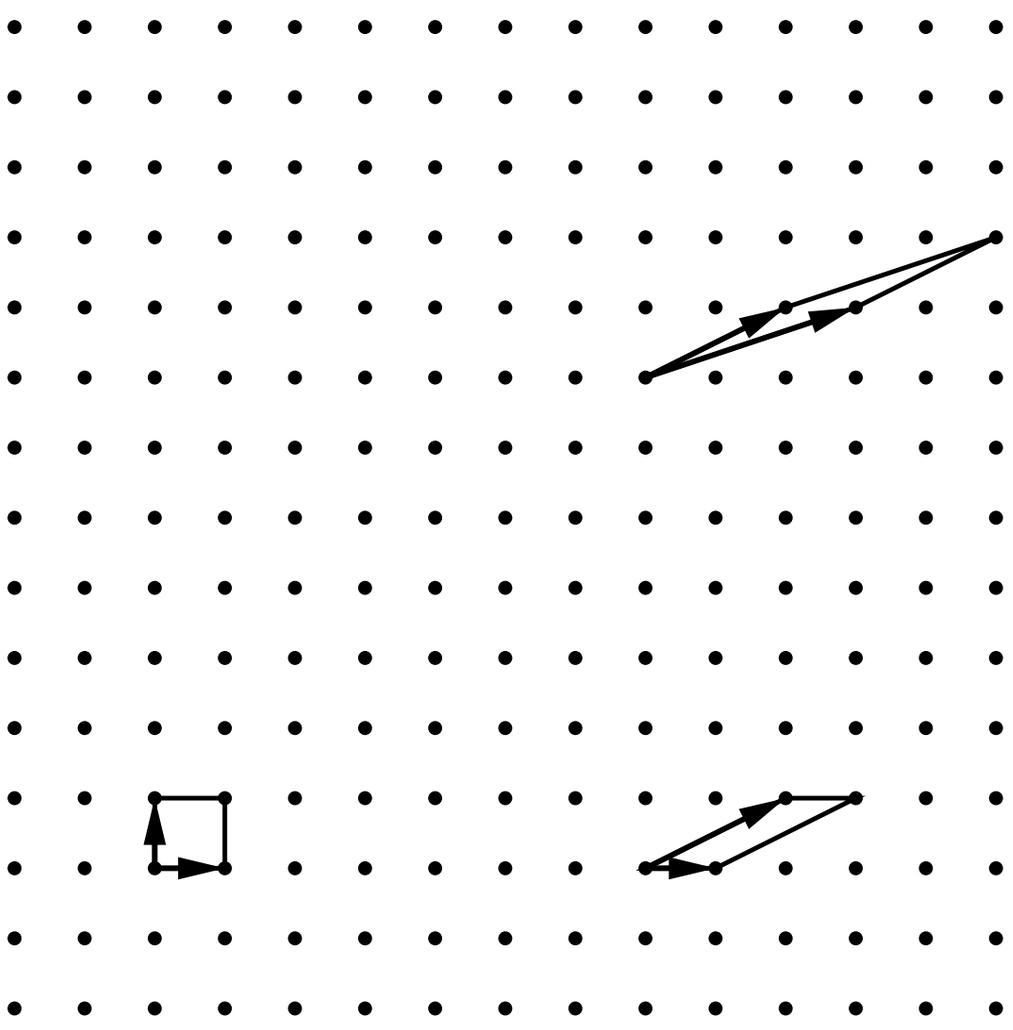
$g_x^{\mathrm{VMC}}(\vec{r})$ $\qquad$ $g_c^{\mathrm{VMC}}(\vec{r})$



R.Q. Hood, M.Y. Chou, A.J. Williamson, G. Rajagopal, R.J. Needs, W.M.C. Foulkes, Phys. Rev. B 57, 8972 (1998)

lattices

$$\mathcal{L}_\mathsf{A} = \left\{ \sum_i n_i \, \mathbf{a}_i \,\middle|\, n_i \in \mathbb{Z} \right\}$$



primitive lattice vectors

$$\mathbf{A} = (\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_d)$$

not unique

canonical choice:
vectors to nearest neighbors
(LLL algorithm)

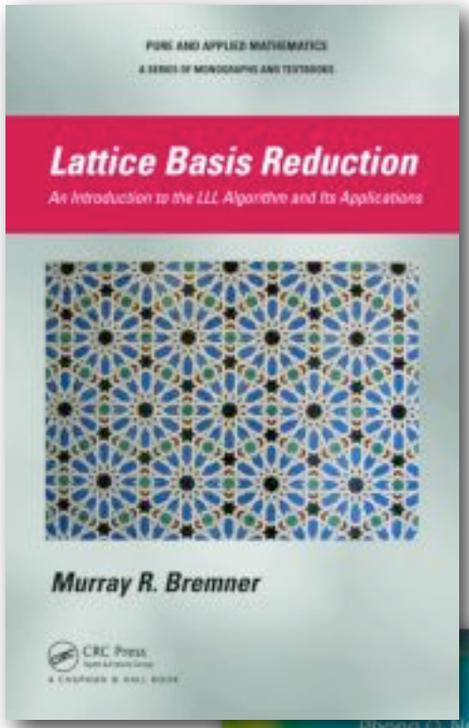
allowed transformations of **A:**

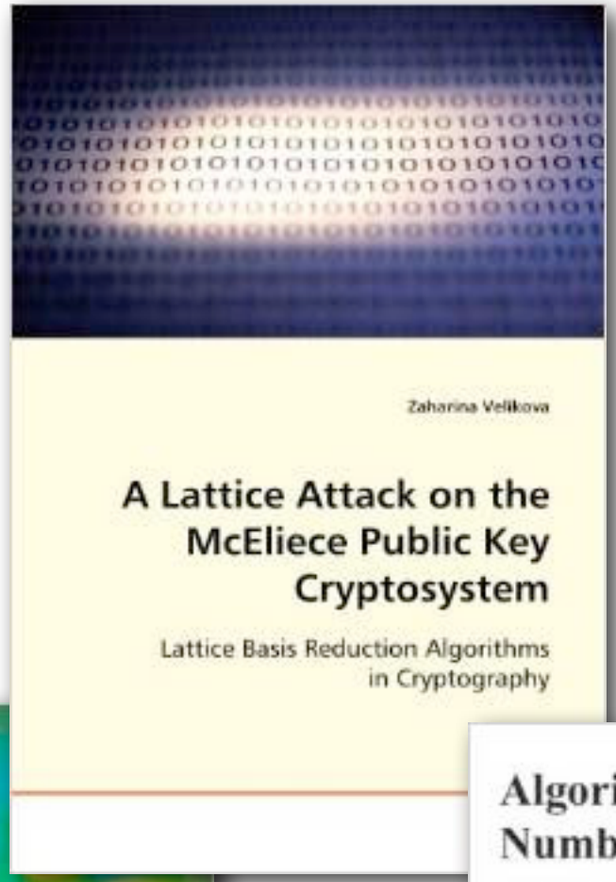
- exchange vectors
- change sign of vector
- add int multiple of other vector

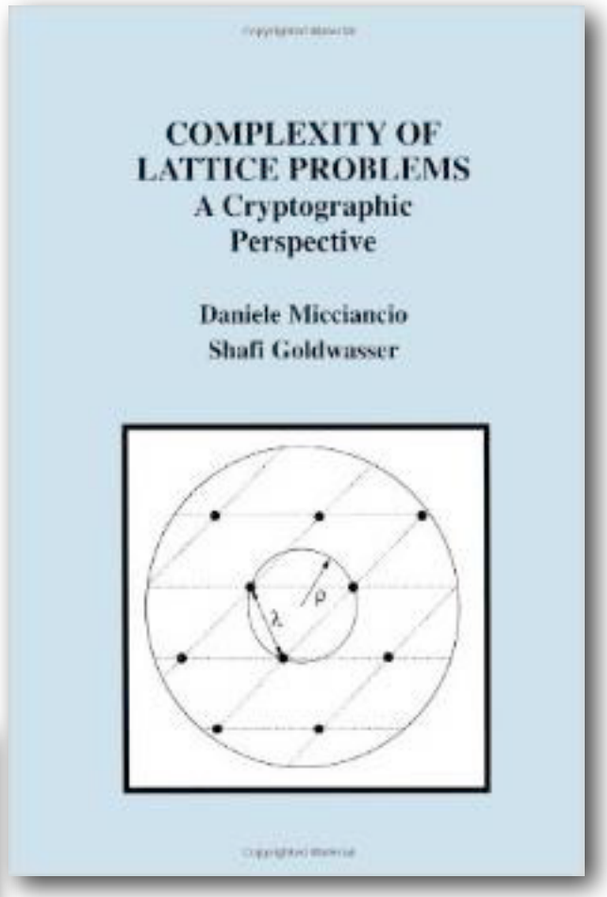
$$\mathcal{L}_\mathsf{A} = \left\{ \mathbf{A}\,\mathbf{n} \,\middle|\, \mathbf{n} \in \mathbb{Z}^d \right\}$$

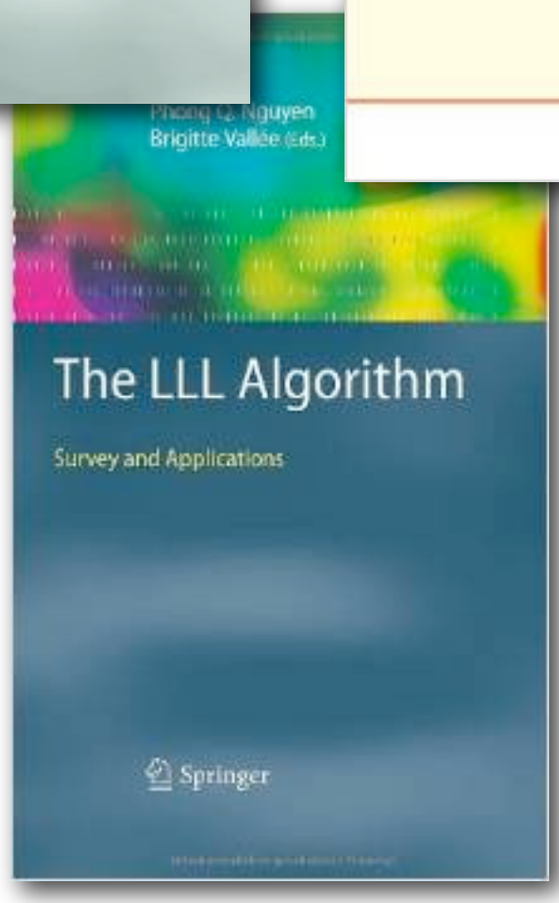
$$V_c = \left| \det(\mathbf{A}) \right|$$

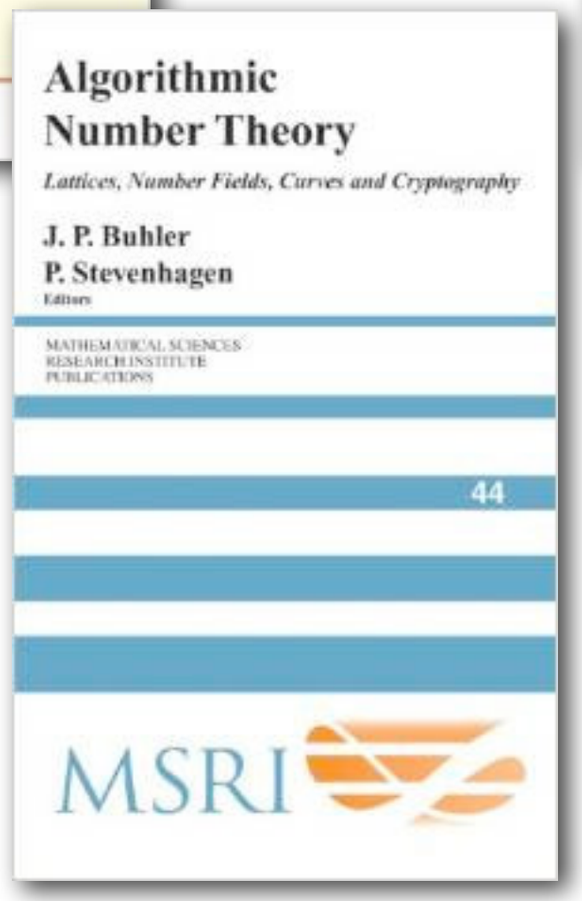
d → ∞ applications to cryptography











SVP
find shortest vector
in lattice

lattice periodic functions

Fourier transform

$$V(\mathbf{r}) = \int d\mathbf{k}\, \hat{V}(\mathbf{k})\, e^{i\mathrm{k}\cdot\mathrm{r}}$$

lattice periodicity

$$V(\mathbf{r}+\mathbf{A}\mathbf{n}) = \int d\mathbf{k}\, \hat{V}(\mathbf{k})\, e^{i\mathrm{k}\cdot\mathrm{r}} \underbrace{e^{i\mathrm{k}\cdot\mathrm{An}}}_{=1} = V(\mathbf{r})$$

only modes that contribute

$$\mathbf{k} \in \left\{ \mathbf{G}\,\mathbf{m} \,\middle|\, \mathbf{m} \in \mathbb{Z}^d \right\} = \mathcal{R}_{\mathcal{L}} \quad \text{with} \quad \mathbf{G} = (2\pi \mathbf{A}^{-1})^T$$

$$\mathbf{G}\,\mathbf{m} \cdot \mathbf{A}\,\mathbf{n} = \mathbf{m}^T \underbrace{\mathbf{G}^T \mathbf{A}}_{2\pi} \mathbf{n} = 2\pi \times \text{integer}$$

Bloch theorem

lattice-periodic potential

$$H_{\text{single}} = \sum_{\mathrm{k}} \frac{\mathbf{k}^2}{2}\, c^\dagger_{\mathrm{k},\sigma}\, c_{\mathrm{k},\sigma} + \sum_{\mathrm{k}} \sum_{\mathrm{m}\in\mathbb{Z}^d} \hat{V}_{\mathrm{Gm}}\; c^\dagger_{\mathrm{k}+\mathrm{Gm},\sigma}\, c_{\mathrm{k},\sigma}$$

eigenstates: Bloch waves

$$\varphi_{n,\mathrm{k}}(\mathbf{r}) = \sum_{\mathrm{m}\in\mathbb{Z}^d} c_{n,\mathrm{m}}\, e^{i(\mathrm{k}+\mathrm{Gm})\cdot\mathrm{r}} \;\rightsquigarrow\; \varphi_{n,\mathrm{k}}(\mathbf{r}+\mathbf{An}) = e^{i\mathrm{k}\cdot\mathrm{An}}\, \varphi_{n,\mathrm{k}}(\mathbf{r})$$

reduce eigenvalue problem to single unit cell with pbc

$$\left(\frac{1}{2}\left(-i\nabla_{\mathrm{r}} + \mathbf{k}\right)^2 + V(\mathbf{r})\right) u_{n,\mathrm{k}}(\mathbf{r}) = \varepsilon_{n,\mathrm{k}}\, u_{n,\mathrm{k}}(\mathbf{r})$$

vector potential

$$\varphi_{n,\mathrm{k}}(\mathbf{r}) = e^{i\mathrm{k}\cdot\mathrm{r}}\, u_{n,\mathrm{k}}(\mathbf{r})$$

many-electron Bloch theorem

$$H = \sum_{\mathrm{k},\sigma} \left(\frac{\mathbf{k}^2}{2}\, c^\dagger_{\mathrm{k},\sigma}\, c_{\mathrm{k},\sigma} + \sum_{\mathrm{m}} \hat{V}_{\mathrm{Gm}}\, c^\dagger_{\mathrm{k+Gm},\sigma} c_{\mathrm{k},\sigma} + \frac{1}{2} \sum_{\mathrm{k}',\sigma';\mathrm{q}} c^\dagger_{\mathrm{k+q},\sigma} c^\dagger_{\mathrm{k}'-\mathrm{q},\sigma'} \frac{1}{|\mathbf{q}|^2}\, c_{\mathrm{k}',\sigma'} c_{\mathrm{k},\sigma} \right)$$

couples all states with given *total* crystal momentum
(invariance under translation of *all* electrons by lattice vector)

to move all electrons into a simulation cell **C**, need to *postulate* Bloch-like theorem

$$\Psi^{\mathrm{C}}_{n,\tilde{\mathrm{k}}}(\mathbf{r}_1, \mathbf{r}_2, \ldots) = e^{i\tilde{\mathrm{k}}\cdot\sum_i \mathrm{r}_i}\, U^{\mathrm{C}}_{n,\tilde{\mathrm{k}}}(\mathbf{r}_1, \mathbf{r}_2, \ldots)$$

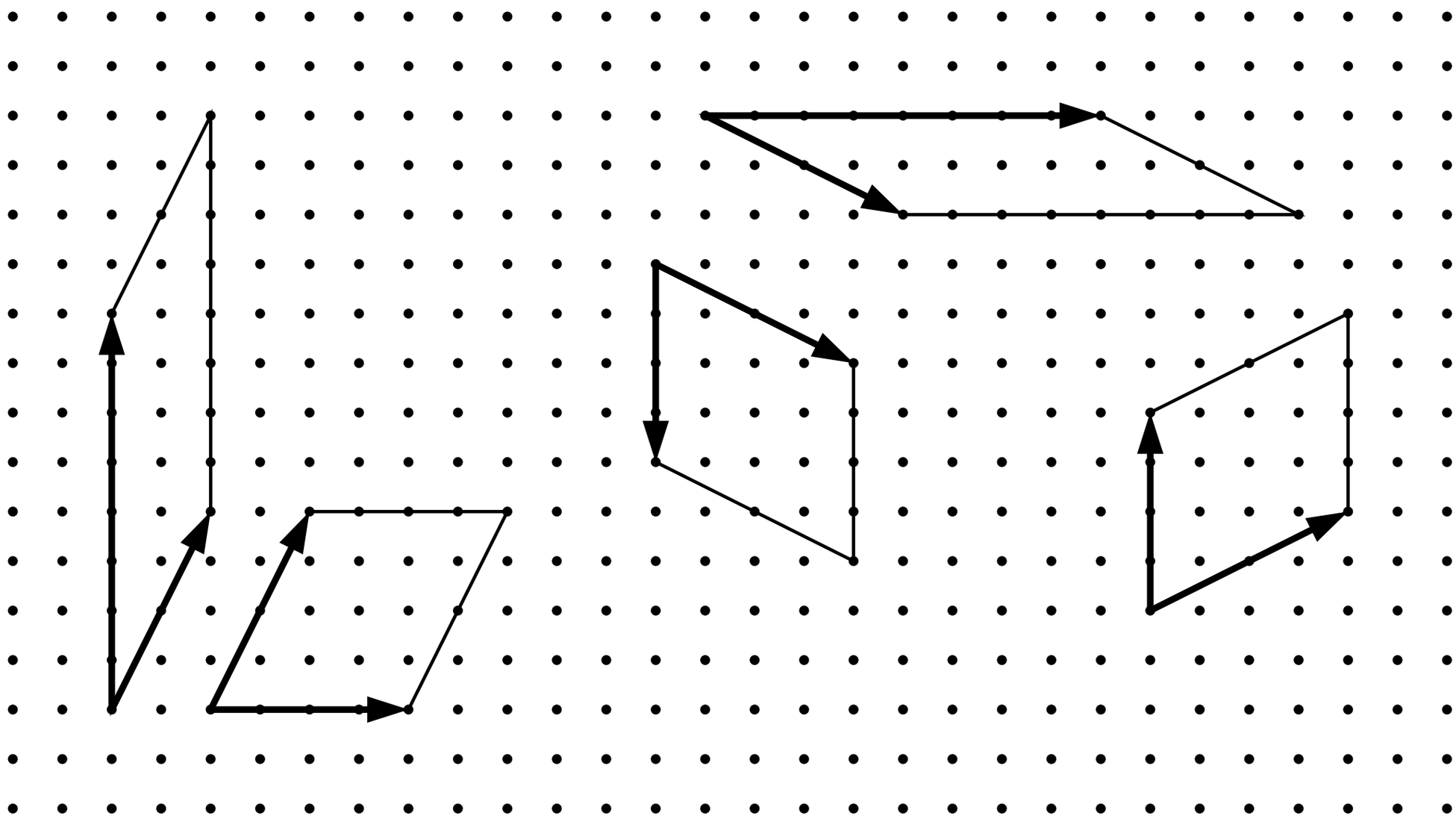
k enters eigenvalue equation for U^{C} as a vector potential

susceptibility $\left.\frac{d^2 E(\mathbf{k})}{d\mathbf{k}^2}\right|_{k=0}$ distinguish metals from (Mott) insulators

Kohn, Phys. Rev. **133,** A171 **(**1964)

supercells

$$\mathbf{C} = \mathbf{A}\,\mathbf{L} \qquad V = \left|\det(\mathbf{C})\right|$$



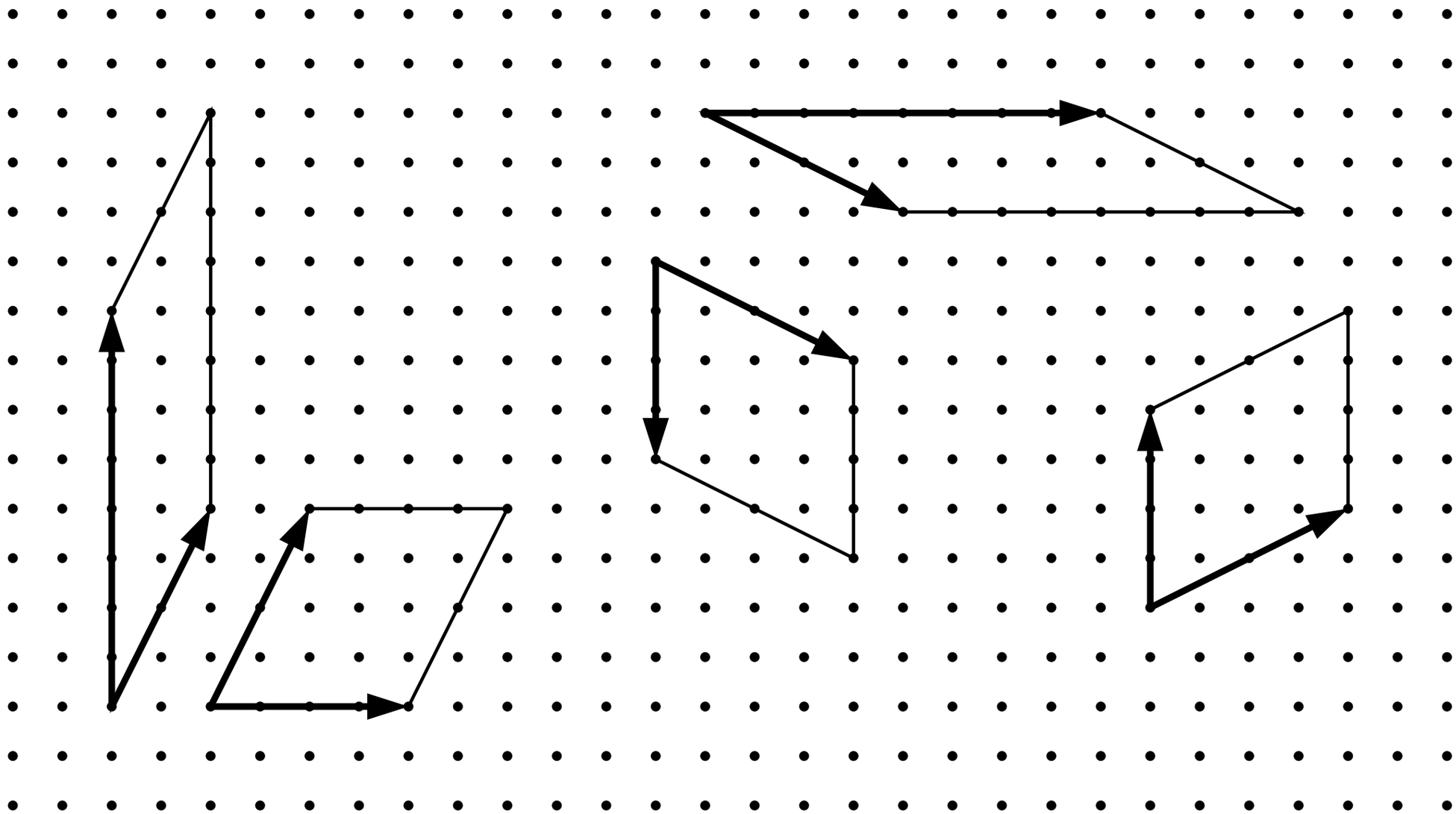
Hermite normal form

$$\mathbf{\Lambda} = \begin{pmatrix} \lambda_{11} & 0 & 0 & \cdots \\ \lambda_{21} & \lambda_{22} & 0 & \\ \lambda_{31} & \lambda_{32} & \lambda_{33} & \\ \vdots & & & \ddots \end{pmatrix} \qquad 0 \le \lambda_{ij} < \lambda_{ii}$$

Euclidean algorithm

$$\gcd(a,b) = \begin{cases} |a| & \text{if } b = 0 \quad \text{(change sign of column)} \\ \gcd(b,a) & \text{if } |a| < |b| \quad \text{(exchange columns)} \\ \gcd(a - \lfloor a/b \rfloor b, b) & \text{otherwise} \quad \text{(add integer multiple of col)} \end{cases}$$

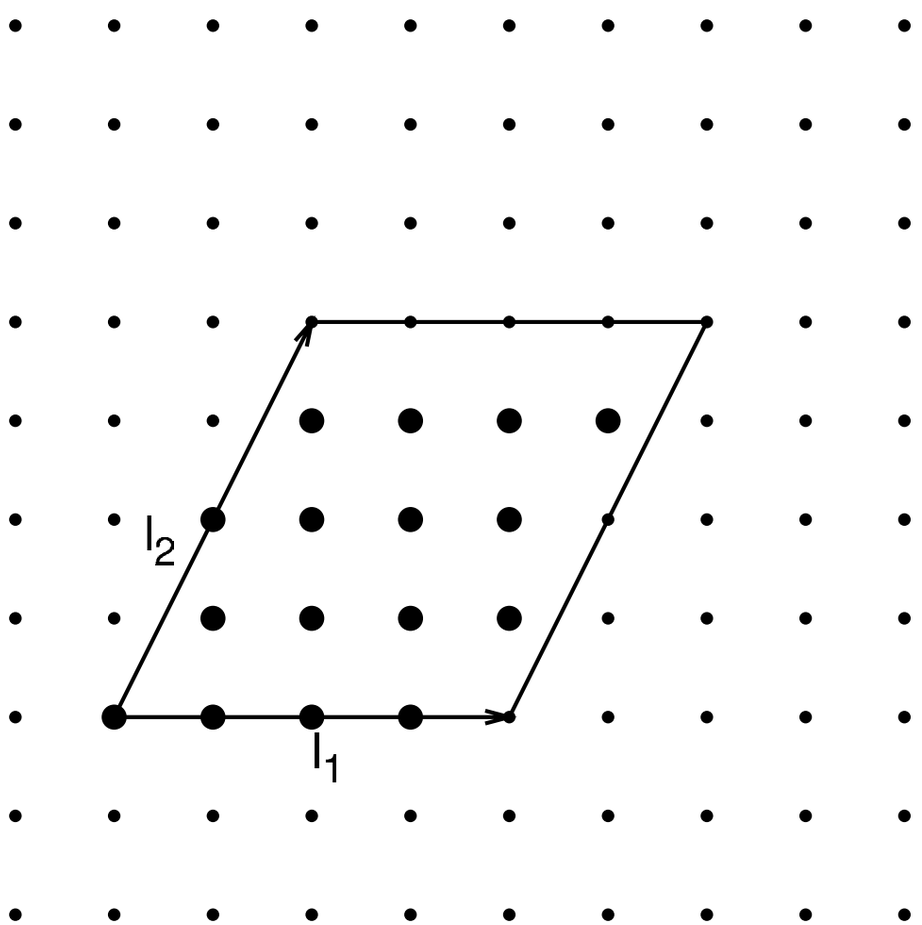
Hermite normal form



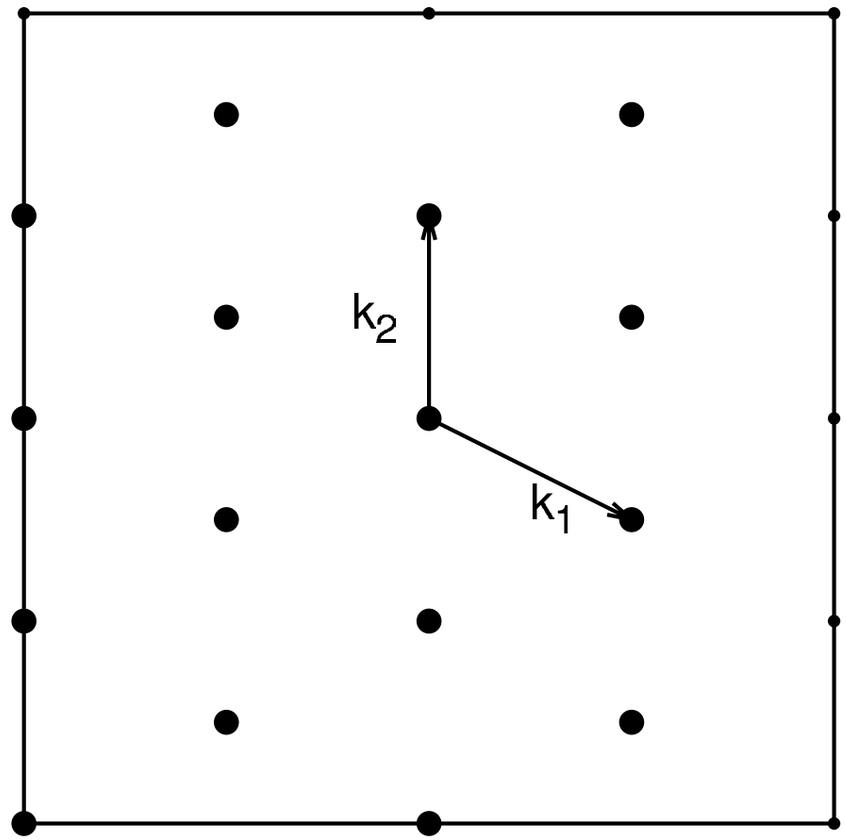
$$\mathbf{L}: \begin{pmatrix} 2 & 0 \\ 4 & 8 \end{pmatrix}_{\text{HNF}} \quad \begin{pmatrix} 4 & 2 \\ 0 & 4 \end{pmatrix} \qquad \begin{pmatrix} 0 & 4 \\ -4 & -2 \end{pmatrix} \quad \begin{pmatrix} 4 & 8 \\ -2 & 0 \end{pmatrix} \quad \begin{pmatrix} 4 & 0 \\ 2 & 4 \end{pmatrix}_{\text{HNF}}$$

supercell: *k*-point sampling

$$\mathbf{K}_{\mathcal{S}} = (2\pi\mathbf{C}^{-1})^T = \mathbf{G}(\mathbf{L}^{-1})^T$$



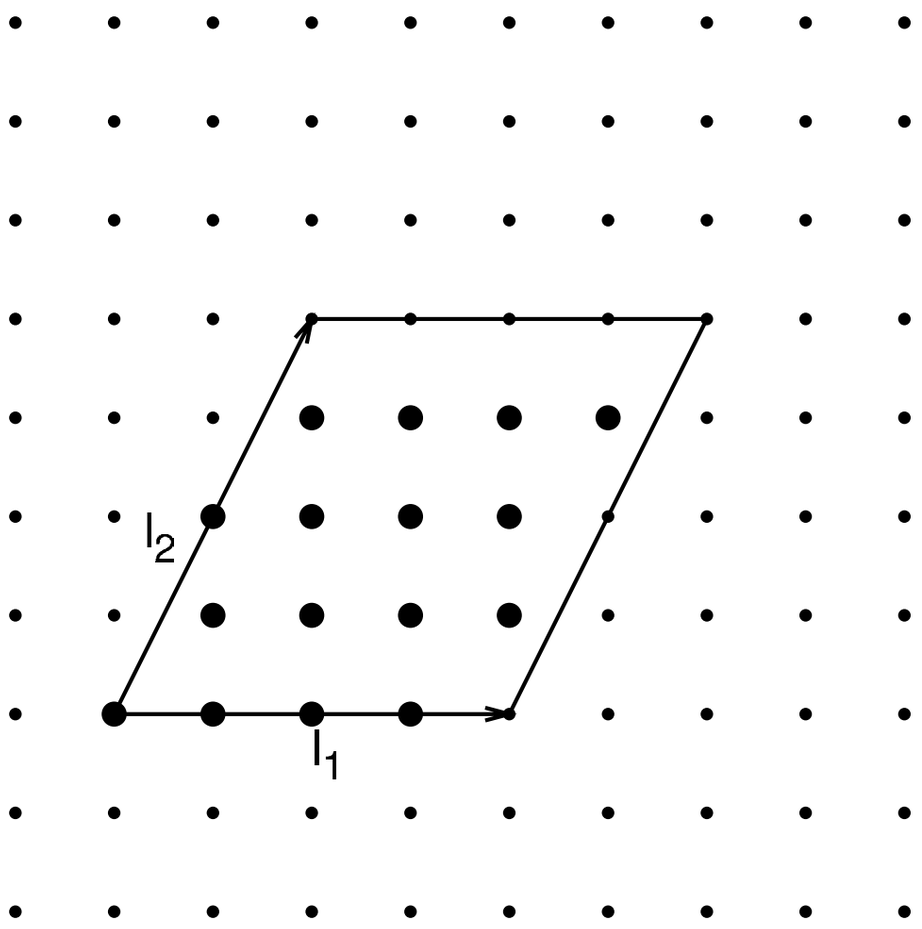
supercell



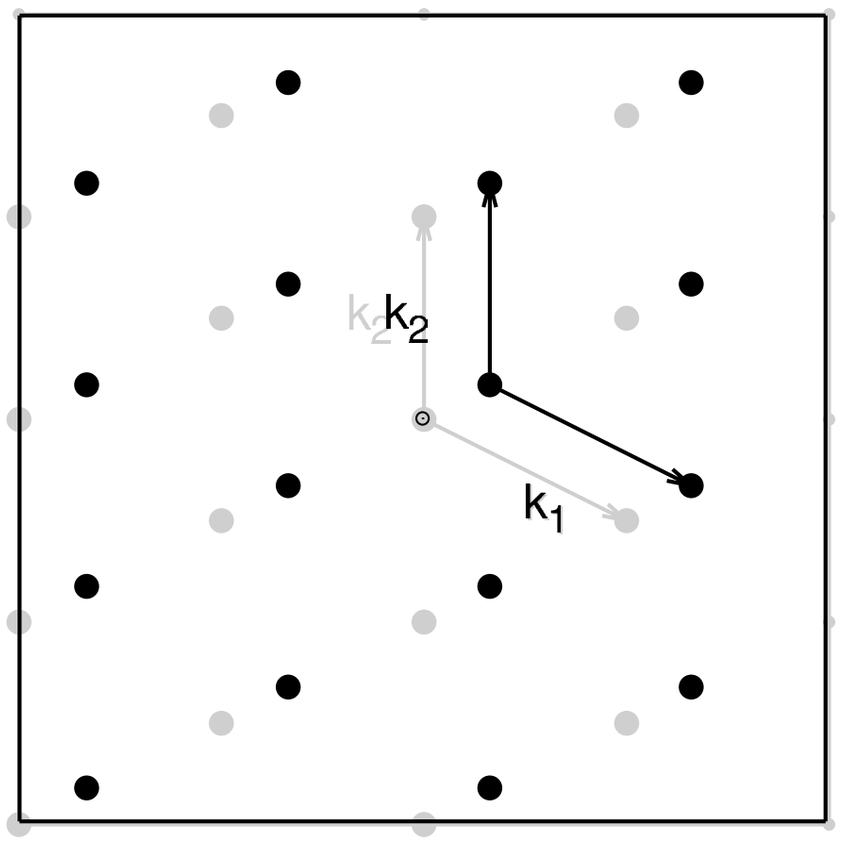
Brillouin zone

supercell: *k*-point sampling

$$\mathbf{K}_{\mathcal{S}} = (2\pi\mathbf{C}^{-1})^T = \mathbf{G}(\mathbf{L}^{-1})^T$$



supercell



Brillouin zone

Monkhorst-Pack grid

particularly suited for Brillouin-zone integrals

$$\mathbf{L} = \begin{pmatrix} n_1 & 0 & 0 \\ 0 & n_2 & 0 \\ 0 & 0 & n_3 \end{pmatrix}$$

$$\tilde{\mathbf{k}} = \sum_i \frac{(n_i - 1)\mathbf{k}_i}{2n_i}$$

PHYSICAL REVIEW B VOLUME 13, NUMBER 12 15 JUNE 1976

Special points for Brillouin-zone integrations*

Hendrik J. Monkhorst and James D. Pack
Department of Physics, University of Utah, Salt Lake City, Utah 84112
(Received 21 January 1976)

A method is given for generating sets of special points in the Brillouin zone which provides an efficient means of integrating periodic functions of the wave vector. The integration can be over the entire Brillouin zone or over specified portions thereof. This method also has applications in spectral and density-of-state calculations. The relationships to the Chadi-Cohen and Gilat-Raubenheimer methods are indicated.

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PR **136**, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB **23**, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL **45**, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR **108**, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL **19**, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB **12**, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
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RMP **54**, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB **13**, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

PR, Physical Review; PRB, Physical Review B; PRL, Physical Review Letters; RMP, Reviews of Modern Physics.

S. Redner: *Citation Statistics from 110 years of Physical Review*
Physics Today June 2005, p. 49

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RMP **57**, 28				
RMP **54**, 43				
PRB **13**, 518				
PR, Physical				

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4	PRL	45	566	(1980)	2514	Ground State of the Electron..	D. M. Ceperley & B. J. Alder
5	PRL	77	3865	(1996)	2478	Generalized Gradient Approx...	Perdew, Burke, Ernzerhof
6	PRB	13	5188	(1976)	2277	Special Points for Brillouin..	H. J. Monkhorst & J. D. Pack
7	PRB	54	11169	(1996)	1933	Efficient Iterative Schemes....	G. Kresse & J. Furthmuller
8	PRB	43	1993	(1991)	1776	Efficient Pseudopotentials for	N. Troullier & J.L. Martins
9	PRB	41	7892	(1990)	1749	Soft Self-Consistent Pseudopotentials...	D. Vanderbilt
10	PR	108	1175	(1957)	1650	Theory of Superconductivity	Bardeen, Cooper, Schrieffer

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Physic

S. Redner: *A Physicist's Perspective on Citation Analysis*
Trends in Research Measurement Metrics, Washington DC, Oct 2010
http://physics.bu.edu/~redner/talks/citations-10.pdf

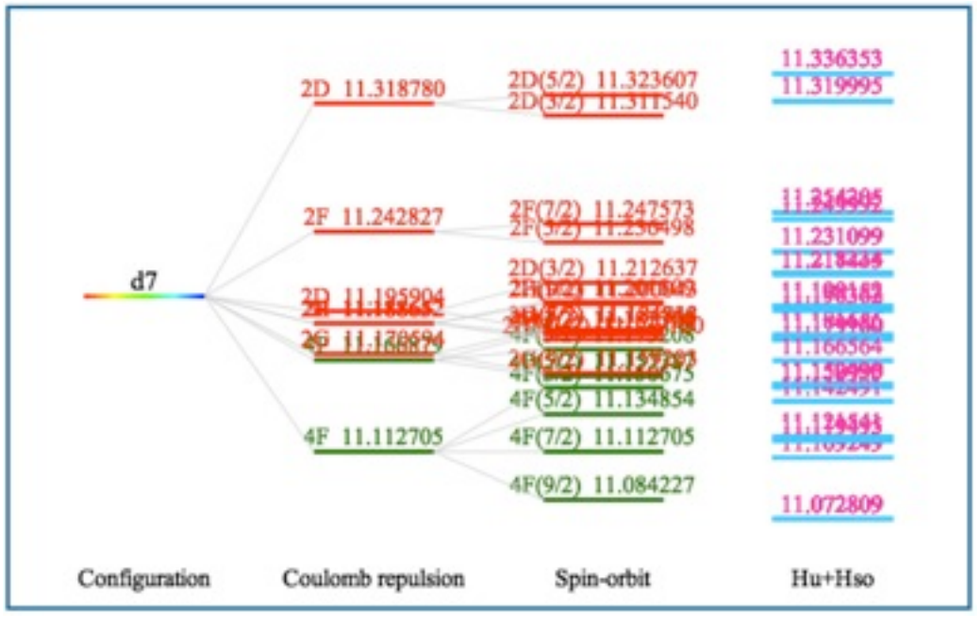
Conclusions

second quantization

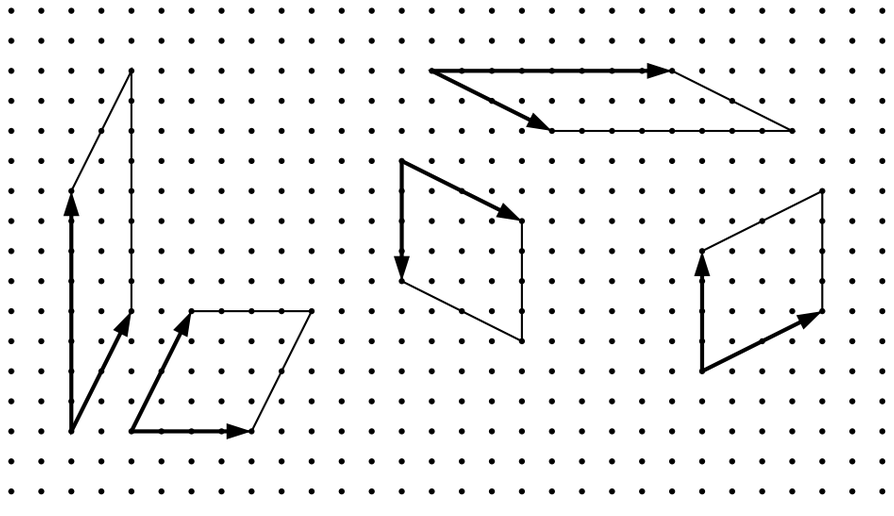
$$c_\alpha|0\rangle = 0 \qquad \{c_\alpha, c_\beta\} = 0 = \{c_\alpha^\dagger, c_\beta^\dagger\}$$
$$\langle 0|0\rangle = 1 \qquad \{c_\alpha, c_\beta^\dagger\} = \langle\alpha|\beta\rangle$$

$$\Phi_{\alpha_1\alpha_2\ldots\alpha_N}(x_1, x_2, \ldots, x_N)$$
$$\rightsquigarrow c_{\alpha_N}^\dagger \cdots c_{\alpha_2}^\dagger c_{\alpha_1}^\dagger |0\rangle$$

degenerate perturbation theory



many-body Bloch supercell &



renormalized models